M. H. Gordon

M H Gordon

A SYSTEMATIC COURSE

OF

QUALITATIVE CHEMICAL ANALYSIS

OF

INORGANIC AND ORGANIC SUBSTANCES

WITH EXPLANATORY NOTES

BY

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poisons, the analysis of urine, and an article on the preparation of reagents.

The final *e* is dropped from the names of halogens and binary compounds, but is retained in the case of the alkaloids so as to avoid confusing them with glucosides. Chemical equations are given for most of the reactions in the inorganic part and for many of the reactions of organic substances, as it is believed that they greatly assist in gaining a clearer insight into chemical action. The author has given credit in the text wherever due, and besides this he acknowledges his indebtedness to the United States Pharmacopœia, Eighth Decennial Revision, and to Prof. Elias H. Bartley and Dr. Joseph Mayer, for their contributions and valued suggestions; and he especially expresses his thanks to Dr. I. V. Stanley Stanislaus for the considerable work he has done in the preparation of this book.

H. W. S.

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QUALITATIVE CHEMICAL ANALYSIS.

PART I.

DEFINITIONS AND GENERAL CONSIDERATIONS.

1. **Matter.**—The substance of which all bodies are constituted is called matter. Examples: Earth, wood, stone, air, vapor, water, etc. There are two kinds of matter, simple and compound.

Matter exists in three states of aggregation; i.e., as solids, liquids, and gases.

2. **Continuity of Matter.**—Whenever a bar of any metal is heated it expands; when cooled it contracts. These changes are most reasonably accounted for by assuming that the metal is composed of minute particles which are not in absolute contact, and which may approach or recede from each other with the withdrawal or application of heat.

This non-continuity is likewise proved when two liquids of different densities are mixed; for example, if 50 cubic centimeters of alcohol are mixed with 50 cubic centimeters of water, the product is not 100 cubic centimeters of mixture, but only 97 cubic centimeters, showing a loss in volume of 3 per cent. This reduction of volume clearly indicates that between the particles of one of the two liquids there must be open spaces which particles of the other liquid have filled up.

There are many other considerations which lead us to

believe that matter is not continuous as it appears to the senses and as generally believed, but is composed of exceedingly small particles which are not rigidly joined together, but are at relatively considerable, though exceedingly minute, distances apart; and that these particles are in a state of perpetual motion, which motion is increased by raising and decreased by lowering the temperature of the mass.

Matter is divided into three general divisions—masses, molecules, and atoms; and it is impenetrable and indestructible.

3. **Mass,** or body, is any distinct portion of matter appreciable by the senses.

Molecules and Atoms.—A *molecule* (a little mass) is "the smallest particle of matter which can exist in a free state".

The small particles referred to in paragraph 2 are called molecules; and masses of matter large enough to be evident to the senses are aggregations of molecules.

All compounds are made up of one or more distinct substances into which they may be split. Since every compound can be split into at least two elements, it follows that its molecule must consist of one particle of each element. Hence there must be particles of matter *smaller* than the molecule itself.

These *smaller* elementary particles, called *atoms*, are defined as "the smallest particle of matter that can enter a chemical combination". Atoms are the constituents of molecules; they are indivisible and indestructible; under ordinary conditions they cannot exist free, but when forced from one combination immediately enter another.

A collection of atoms forms a molecule, and a collection of molecules forms a mass.

The molecules of compounds may consist of any number of atoms; molecules of elements usually of only two.

4. **Elements and Compounds.**—As stated in paragraph 1, there are two kinds of matter, the simple and the compound.

Simple matter consists of only one elementary substance, as iron, lead, oxygen, carbon. Compound matter is com-

posed of two or more kinds of matter in combination, as iron oxid, which consists of iron and oxygen; and lead sulfate, which consists of lead, sulfur, and oxygen.

Simple matter cannot be reduced to anything simpler by any known means; it is therefore assumed to consist of but one kind of matter, and is called an *element*.

About seventy-four different kinds of elementary matter, or so-called elements, are now known, and it is almost certain that others remain to be discovered. Out of these elementary substances the entire universe is constructed.

The list of compounds, constantly increasing, is innumerable.

5. **Definition of Chemistry.**—Chemistry is the science which considers the composition of substances and changes of composition which they may undergo.

Practically, the study of chemistry consists in subjecting materials to the action of certain substances called "reagents", or to the action of heat, light, or electricity, and noting the changes which may occur. These changes are called "reactions".

Chemistry deals with the atoms composing the molecules. It studies the properties of atoms, their association into molecules, their mutual attraction, the changes of their positions on the application of various forces, the compounds they form when brought together with other atoms or molecules, etc.

6. **Inorganic and Organic Chemistry.**—By Inorganic Chemistry we mean "the study of the compounds of mineral origin". By Organic Chemistry is meant the study of the compounds formed in the tissues of plants or animals, and other "organized" compounds. It is usually defined as "the chemistry of carbon compounds".

7. **Chemical and Physical Change.** — Our knowledge of things is derived mostly by observing their *specific properties*, such as color, hardness, fluidity, transparency, odor, etc., and the changes which take place in them.

These changes are comprised under two general headings, viz., physical changes and chemical changes.

A physical change is one in which the composition and properties of a substance are *not permanently* altered.

A chemical change is one in which both composition and properties are *permanently* altered and one or more new substances produced.

To illustrate the above-mentioned changes we will take common salt. It is a solid; when put into water it dissolves—a *physical* change occurs; now we apply heat, vaporize the water, and recover the original solid—unchanged common salt. If we now take the same salt and dissolve it in sulfuric acid, a *chemical* change takes place, and the products of this change, hydrochloric acid and sodium sulfate, are entirely unlike the common salt from which they were formed. The acid and the new salt formed are new *compounds* produced by a chemical change.

8. Compounds and Mechanical Mixtures.—These should be differentiated: In a mechanical mixture there is no true union of the elements; in a compound there is. As an example we will take iron and sulfur. Reduce the iron in a mortar to the finest possible powder; do likewise with the sulfur; now mix the powders intimately until the mixture presents a uniform appearance. Place a small quantity of it under a microscope and small particles of iron and sulfur lying side by side will be revealed.

Now if another portion of the mixture is taken and heated to redness, a chemical change occurs, a true compound is formed, in which neither the iron nor the sulfur can be revealed under the microscope.

Before heating, therefore, the powder was but a mechanical mixture, but after heating a true chemical compound, iron sulfid, is found to have been produced.

9. Molecular Attraction and Chemism.—Molecules attract one another. When the molecules are of the same kind they

form a homogeneous mass, and the force acting between them is called *cohesion.* When the molecules are not of the same kind the force of attraction is called *adhesion.* A piece of lead thrust into water comes out wet because of the water adhering to it. Try now to pull the lead apart to smaller pieces: you cannot, because cohesion keeps it together. *Chemism* is to molecules what cohesion is to masses. It is the force which attracts atoms to one another to form molecules.

10. **Atomic and Molecular Weights.**—The atoms possess definite weights of their own. The atomic weight of any element is the number of times its atom is heavier than the atom of hydrogen, which, being the lightest substance known, is generally used as the standard of weight. Its atomic weight is taken as *one;* that is, it weighs one *microcrith.*

When, for example, oxygen is said to have the weight of 16, it is understood that its atom has a weight of 16 microcriths, or that it weighs 16 times as much as the hydrogen atom. Thus we say nitrogen weighs 14, carbon 12, sodium 23, calcium 40, etc. Molecular weight is the sum total of the atomic weights in a molecule of a substance. Thus the molecular formula of calcium carbonate is $CaCO_3$; that is, it is composed of one atom of calcium having the weight of 40, one atom of carbon weighing 12, and three atoms of oxygen each weighing 16, or 48 for the three. Adding these atomic weights $(40+12+48)$ together we get the sum of 100, which is the molecular weight of the calcium carbonate, or common chalk.

11. **Valence, also called Quantivalence, or "Bonds".**—By the "valence" of an element is meant "the combining power of one of its atoms as compared with that of hydrogen". As will be seen, hydrogen is also the "unit" of valence, as it is of weight.

Atoms of certain elements, such as chlorin, are found to be equal in *combining* power to those of hydrogen; i.e., one atom of chlorin unites with one atom of hydrogen. Hydrogen being

the unit has the valency of 1, or one bond; it is also called a "monad," or a "univalent" element.

When it is said that oxygen has the valency of 2, or that oxygen is a dyad, it is meant that the combining value of its atoms is twice that of the hydrogen atom, and that in order to make these two combine two atoms of hydrogen must be employed to satisfy one atom of oxygen, thus: $\left.\begin{matrix}H\\H\end{matrix}\right\rangle O = H_2O$. Nitrogen, having the valence of 3, is a triad, and requires 3 atoms of hydrogen to satisfy its atom, thus: $N\!\begin{matrix}\diagup H\\ - H\\ \diagdown H\end{matrix} = NH_3$.

From the above we will see that the chemical value of any atom is equal to that of another atom which can replace it in a molecule. Thus atoms are divided into monads, dyads, triads, tetrads, pentads, hexads, heptads, etc., according as they can replace 1, 2, 3, 4, 5, 6, or 7 atoms of hydrogen or its equivalent in a molecule.

An element, while it always has the same valence in the same compound, may have different valences in different compounds or combinations. In ammonia (NH_3), for example, the valence of nitrogen is always 3, but in nitrogen pentoxid (N_2O_5) it is always 5; many other elements have this *variable valence.*

A monad	is	equivalent	to a monad.		
" dyad	"	"	" 2	monads or 1 dyad.	
" triad	"	"	" 3	"	" 1 monad and 1 dyad.
" tetrad	"	"	" 4	".	" 2 dyads or 1 monad) and 1 triad.
" pentad	"	"	" 5	"	" 1 tetrad and 1 monad,
					" 1 triad and 2 monads,
					" 2 dyads and 1 monad.

The valence of an atom is often indicated by accents placed to the right of its symbol, thus: H′, H‴; or by Latin numerals, as O^{II}, C^{IV}, etc.

Notation, Classification, and Nomenclature of Elements and Inorganic Compounds.

12. **Symbols.**—For convenience in writing chemical reactions and for many other reasons, certain symbols are used which represent or stand for the names of elements. These symbols are the initials of their Latin names (H for hydrogen, O for oxygen, N for nitrogen, S for sulfur, etc.). When more than one element has a name beginning with the same letter, another characteristic letter is added. The first letter is always a capital, the second is small (Hg for hydrargyrum, Os for osmium, Ni for nickel, Sb for stibium, etc.). *Each symbol* stands for *one atom* of the element, unless a figure is attached to the upper or lower right-hand corner, which indicates a greater number of atoms: $H'=1$ atom of hydrogen, $H_2=2$ atoms of hydrogen.

13. **Metals are Classified** according to their chemical and physical relationship. The "Periodic System" groups the elements progressively in accordance with their atomic weights, thus exhibiting these relationships most perfectly.

The arrangement used in this book groups the elements most advantageously for the practical work of the chemist.

The following tables include the most important elements and acids. Students would do well to study carefully and commit to memory the grouping, symbols, and valences.

In Table I we will find the *Non-Metals* classified. These may be solid, liquid, or gaseous at ordinary temperatures. They have no lustre, ductility, or malleability, are poor conductors of heat and electricity, and are electronegative in combinations. They are the *Acid-forming Elements*.

In Table II we find the *Metals*, or *Base-forming Elements*. These are electropositive, solid (except mercury) at ordinary temperatures; generally heavy bodies, good conductors of heat and electricity, and possessing more or less lustre.

In Table III the *Acids* are grouped according to their valence or basicity.

An acid is defined as a "salt of hydrogen". In reality "acids are the hydroxids of the non-metals", and while *not* all the acids contain oxygen, every acid contains hydrogen.

Acids containing oxygen are called *oxacids*, of which nitric acid (HNO_3) is an example; those in which oxygen is wanting are classed as *hydracids;* thus hydrochloric acid (HCl) is a hydracid.

An acid consists of two parts: *Replaceable* or *basic hydrogen*, and the *acidulous radical* The hydrogen may be replaced by a metal, and the acid radical may pass into another compound without splitting into its elements. The basicity or valence of an acid is determined by the number of replaceable hydrogen atoms it contains; thus, H(Cl) is a monobasic acid, $H_2(SO_4)$ is a dibasic acid, $H_3(PO_4)$ is a tribasic acid, etc.; the acidulous radicals are in parenthesis.

14. TABLE I.—NON-METALS.

Grouping.	Symbol.	Valences.	Atomic Weights.
Hydrogen Group:			
Hydrogen	H	1	1.0
Chlorin Group:			
Chlorin	Cl	1, 3, 5	35.37
Bromin	Br	1, 3, 5	79.76
Iodin	I	1, 3, 5	126.53
Fluorin	F	1	19.0
Sulfur Group:			
Oxygen	O	2	15.96
Sulfur	S	2, 4, 6	31.98
Selenium	Se	2, 4, 6	79
Tellurium	Te	2, 4, 6	128
Nitrogen Group:			
Boron	B	3	10.9
Nitrogen	N	3, 5	14.01
Arsenic	As	3, 5	74.9
Antimony	Sb	3, 5	119.6
Phosphorus	P	3, 5	30.96
Carbon Group:			
Carbon	C	2, 4	11.97
Silicon	Si	2	28.3

15. TABLE II.—THE METALS.

	Grouping.	Symbol.	Valence in *-ous* compounds.	Valence in *-ic* compounds.	Atomic. Weight
Metals precipitated, by dilute HCl, whose chlorids, sulfids, hydroxids, and carbonates are insoluble in H_2O.	*First Group:*				
	Silver..........	Ag		1	107.66
	Lead...........	Pb		2	206.4
	Mercurosum....	Hg″	1	....	199.8
Metals precipitated by H_2S in acid solution, whose sulfids are soluble in $(NH_4)_2S$.	*Second Group—First Division:*				
	Arsenic.........	As	3	5	74.9
	Antimony......	Sb	3	5	119.6
	Tin............	Sn	2	4	118.8
Metals precipitated from acid solution by H_2S, whose sulfids are insoluble in $(NH_4)_2S$.	*Second Group—Second Division:*				
	Bismuth........	Bi	3	5	208.9
	Copper.........	Cu	1	2	62.18
	Mercuricum.....	Hg		2	199.8
	Cadmium.......	Cd		2	111.5
Metals not precipitated by H_2S from acid solutions but precipitated by $(NH_4)_2S$ as sulfids.	*Third Group—First Division:*				
	Iron...........	Fe	2	3	55.88
	Cobalt.........	Co	2	3	59.0
	Nickel.........	Ni	2	3	58.6
	Manganese.....	Mn	2	3	54.8
	Zinc...........	Zn		2	65.1
Metals not precipitated by H_2S from acid solutions but precipitated by $(NH_4)_2S$ as hydroxids.	*Third Group—Second Division:*				
	Aluminum......	Al		3	27.04
	Chromium......	Cr	2	3	52.0
Metals not precipitated by sulfids, either from acid or alkaline solution, but precipitated by carbonates	*Fourth Group:*				
	Calcium........	Ca		2	40.0
	Strontium......	Sr		2	87.3
	Barium.	Ba		2	136.9
	Magnesium.....	Mg		2	24.3
Metals not precipitated by any general reagent.	*Fifth Group:*				
	Lithium........	Li		1	7.01
	Sodium........	Na		1	23.0
	Potassium......	K		1	39.03
	Ammonium.....	NH_4		1	18.0

16. TABLE III.—THE ACIDS.

INORGANIC HYDRACIDS.

	Name of Acid.	Chemical Formula.	Name of its Salt.
Monobasic:	Hydrochloric.	HCl	Chlorid
"	Hydrobromic.	HBr	Bromid
"	Hydriodic.	HI	Iodid
"	Hydrofluoric.	HF	Fluorid
"	Hydrocyanic.	HCN	Cyanid
Dibasic:	Hydrosulfuric.	H_2S	Sulfid
Tribasic:	Hydroferricyanic.	H_3FeCN_6	Ferricyanid
Tetrabasic:	Hydroferrocyanic.	H_4FeCN_6	Ferrocyanid

INORGANIC OXACIDS.

Monobasic:	Chloric.	$HClO_3$	Chlorate
"	Bromic.	$HBrO_3$	Bromate
"	Iodic.	HIO_3	Iodate
"	Nitrous.	HNO_2	Nitrite
"	Nitric.	HNO_3	Nitrate
Dibasic:	Sulfurous.	H_2SO_3	Sulfite
"	Sulfuric.	H_2SO_4	Sulfate
"	Thiosulfuric.	$H_2S_2O_3$	Thiosulfate
"	Carbonic.	H_2CO_3	Carbonate
"	Chromic.	H_2CrO_4	Chromate
Tribasic:	Phosphoric.	H_3PO_4	Phosphate
"	Arsenous.	H_3AsO_3	Arsenite
"	Arsenic.	H_3AsO_4	Arsenate

ORGANIC OXACIDS.

Monobasic:	Formic.	$HCHO_2$	Formate
"	Acetic.	$HC_2H_3O_2$	Acetate
"	Lactic.	$HC_3H_5O_3$	Lactate
"	Benzoic.	$HC_7H_5O_2$	Benzoate
"	Salicylic.	$HC_7H_5O_3$	Salicylate
"	Valerianic.	$HC_5H_9O_2$	Valerianate
Dibasic:	Malic.	$H_2C_4H_6O_5$	Malate
"	Oxalic.	$H_2C_2O_4$	Oxalate
"	Succinic.	$H_2C_4H_4O_4$	Succinate
"	Tartaric.	$H_2C_4H_4O_6$	Tartrate
Tribasic:	Citric.	$H_3C_6H_5O_7$	Citrate
"	Meconic.	$H_3C_7HO_7$	Meconate

17. Importance of Symbols.—The symbols in Tables I and II represent not merely the name of the element, but also a definite weight of the latter. Thus the symbol O represents not merely oxygen, but it stands for one atom of oxygen or 16 parts by weight; N represents one atom of nitrogen or 14 parts by weight; and C represents 12 parts by weight of carbon.

A *Formula* is an expression representing the composition of a molecule; it consists of two or more symbols written together, and therefore represents a definite weight, the molecular weight, which is the sum of the atomic weights of the constituent atoms.

Thus H_2O is the formula which represents water; its molecular weight is 18, i.e., 2 parts by weight of hydrogen and 16 parts by weight of oxygen. NaCl is the formula for sodium chlorid, and represents 58.4 parts by weight of sodium chlorid; 23 for the sodium and 35.4 for the chlorin. KOH is the formula for potassium hydroxid, and represents one atom of potassium, one of oxygen, and one of hydrogen, having the weights 39, 16, and 1 respectively. Hence KOH represents 56 parts by weight of potassium hydroxid.

When we wish to represent more than one atom, we place a small numeral at the right-hand lower corner of the symbol; thus O_2 represents 2 atoms of oxygen, or 32 parts by weight; in the same way K_3 = three atoms of potassium, B_4 = four atoms of boron.

When we wish to represent more than one molecule, we place a large numeral before the formula. Thus 2KOH represents two molecules of KOH; the 2 multiplies each of the atoms in the molecule. $3H_2SO_4$ represents three molecules of H_2SO_4; thus it means, $6\times H$, $3\times S$, and $12\times O$. The three placed before the molecule multiplies the whole molecule; the smaller numerals in this case, 2 and 4, multiply only the atoms which immediately precede them; thus the H is multiplied by 2, and the O by 4.

If a group of symbols is inclosed in a parenthesis and a small numeral placed after it, as in $(NH_4)_2$ and $(SO_4)_3$, the whole group is multiplied by the numeral.

As symbols always represent atomic weights, so formulas represent molecular weights; thus the molecular weight of sodium sulphate, Na_2SO_4, is: Na_2 $(23\times 2) = 46$, $S = 32$, O_4 $(16\times 4) = 64$, which added together give 142.

Equations are representations, by means of symbols, of chemical reactions. Example:

Na_2CO_3	+	$2HCl$	=	$2NaCl$	+	H_2O	+	CO_2.
Sodium Carbonate.		Hydrochloric Acid.		Sodium Chlorid.		Water.		Carbon Dioxid.
$Na_2(23\times2)=46$		$2H=\ 2$		$2Na=46$		$2H=\ 2$		$C=12$
$C \qquad =12$		$2Cl=70.8$		$2Cl=70.8$		$O=16$		$O_2=32$
$O_3(16\times3)=48$								
106		72.8		116.8		18		44

This equation indicates that sodium carbonate treated with hydrochloric acid will yield sodium chlorid, water, and carbon dioxid. There are one molecule of Na_2CO_3 and two molecules of HCl reacting, and producing two molecules of NaCl and one molecule each of H_2O and CO_2.

Now since symbols represent definite weights, an equation can be easily reduced to figures. The atomic weights of the elements entering into the foregoing equation are $Na=23$, $C=12$, $O=16$, $H=1$, and $Cl=35.4$.

Thus we have 106 parts of Na_2CO_3 reacting with 72.8 parts of HCl and forming 116.8 parts of NaCl, 18 parts of H_2O, and 44 parts of CO_2.

In an equation, the sum of the atoms on one side of the sign of equality [=] should equal that on the other.

18. **Classification of Compounds.**—Compounds are classified as *bases*, *acids*, and *salts*.

Bases are the hydroxids of the metals. Slaked lime is the commonest example of this class. Some of the bases are soluble, others not; when soluble they have a caustic taste and turn red litmus blue.

Acids are the salts of hydrogen; these are fully defined in paragraph 13 and classified in Table III. When soluble they have a sharp, sour taste and turn blue litmus red.

Salts are acids in which part or all the basic hydrogen has been replaced by a metal; thus, if the hydrogen of sulfuric acid is replaced by potassium, we have formed a salt, called potassium sulfate; if the hydrogen of acetic acid be replaced by potassium, we have a salt called potassium acetate.

The salts are further classified into *normal, acid, basic,* and *double* salts.

A *normal* salt is one in which all the basic hydrogen has been replaced by a metal, as in Na_2CO_3, sodium carbonate.

An *acid* salt is one in which some of the basic hydrogen still remains, as in $NaHCO_3$, sodium acid carbonate.

A basic salt is a substitution of a metal in part for the H of an acid, and in part for the half or the whole of the H of water; i.e., a basic salt is a compound partly of the nature of a salt and partly of the nature of a hydroxid or an oxid.

Double salt is one in which the basic H of an acid is replaced by more than one metal. Example, $KNaC_4H_4O_6$.

The Names of Acids.—All the names of hydracids begin with *hydro* and end in *ic,* as *hydro*chlor*ic*, *hydro*iod*ic*, *hydro*brom*ic*, etc.

In the oxacids, the quantity of oxygen present in acids of the same element determines their names, thus: acids containing the least amount of oxygen begin with *hypo* and end in *ous;* those containing the next larger quantity of oxygen end in *ous,* omitting the *hypo;* those containing the next larger quantity of oxygen end in *ic.* If there is a fourth acid containing still more oxygen than the preceding one, its name begins with *per* and ends in *ic.* In this way we derive a table of the nomenclature of the acids. Following is a table of the chlorin oxacids:

Formula.	Name of Acid.
$HClO$	Hypochlorous
$HClO_2$	Chlorous
$HClO_3$	Chloric
$HClO_4$	Perchloric

The Names of Salts.—The names of salts also indicate their composition, both as regards their constituents and the quantities of these present in them.

The names of salts generally consist of two words, the first expressing the metal, the second expressing the acid radical; thus, sodium sulfate = Na_2SO_4; zinc chlorid = $ZnCl_2$. The above is true only with the normal salts. In the case of acid or basic salts three and more words are required to express their name and composition, as in potassium acid carbonate, $KHCO_3$, etc.

As is seen in the above, the prefixes and suffixes employed in expressing the names of the acids and salts have a very important meaning, which the following further explains:

The prefix *sesqui* is used to express a proportion of 1 to $1\frac{1}{2}$, as in Fe_2O_3, iron *sesqui*oxid. Prefix *sub*, when used, indicates a lower amount of an element than the name would otherwise represent; thus, Cu_2O, copper *sub*oxid.

The prefix *per* or *hyper* or *super* (above) indicates the *highest* of a series of compounds, as contrasted with *sub* or *hypo*, indicating *lowest*. Examples: $KClO_4$, potassium *per*chlorate; Fe_2Cl_6, iron *per*chlorid.

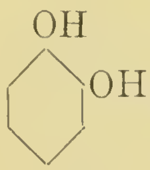
The prefix *ortho* (straight) is used to distinguish normal acids or salts. Example, H_3PO_4, *ortho*phosphoric acid.

The prefix *pyro* (by fire) is used to designate that the body has been produced by heat (fire). Thus $2H_3PO_4$ or $H_6P_2O_8$ + heat becomes $H_4P_2O_7$, pyrophosphoric acid, water (H_2O) being driven out. $C_7H_6O_5$, gallic acid, heated, becomes $C_6H_6O_3$, pyrogallic acid, CO_2 being driven out.

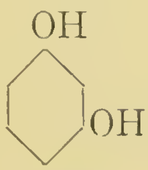
The prefix *meta* is used to designate an altered condition as distinguished from the ortho and pyro (and para) forms. Thus $H_4P_2O_7$ + heat becomes $2HPO_3$, metaphosphoric acid, water being driven out.

The prefixes *ortho*, *meta*, and *para* (near to) are used with organic compounds in which some of the constituent radicals are attached in certain relation to each other; these compounds

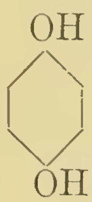
have the same chemical composition but differ in physical properties. The following examples illustrative of this show a difference in the place of attachment of the OH radicals; the chemical composition $C_6H_4(OH)_2$ being the same in each.



is *ortho*-dihydroxybenzol, or pyrocatechin.



is *meta*-dihydroxybenzol, or resorcin.



is *para*-dihydroxybenzol, or hydroquinone.

Para also indicates molecular aggregations of certain organic compounds, as C_2H_4O = aldehyd; and $(C_2H_4O)_3$ or $C_6H_{12}O_3$ = *par*aldehyd.

The prefix *hydro* indicates binary compounds or acids, as *hydro*chloric acid, HCl, *hydro*sulfuric acid, H_2S, etc.

The prefixes *an* (without) and *de* (away from) are used to denote something which has been removed from a body in which it normally exists. Examples: *an*hydrous, without water or moisture; *de*odorized, deprived of odor.

The nomenclature of salts corresponds to that of the acids; thus the name of

a salt of an *hypo* . . .	*ous* acid	begins with *hypo*	and ends in *ite*
" " " "	*ous* acid		ends in *ite*
" " " "	*ic* "		" " *ate*
" " " a *per* . . .	*ic* "	begins with *per*	and ends in *ate*.

The following table of the chlorin oxacids with sodium illustrates this:

Name of Acid.			Name of the Salt.
Hypochlorous acid	forms	Sodium	*Hypo*chlor*ite*
Chlorous "	"	"	Chlor*ite*
Chloric "	"	"	Chlor*ate*
Perchloric "	"	"	*Per*chlor*ate*

For nomenclature of other salts see Table III. The name of a compound may also be varied in other ways to indicate its composition, as *di-sodium phosphate*, Na_2HPO_4, to indicate that only two atoms of basic hydrogen in phosphoric acid, H_3PO_4, have been replaced by the metal. By referring to Table II we note that many elements, as iron, bismuth and arsenic, form two or more classes of compounds corresponding to their *varied valences*.

Names of these compounds in which the element has the lower valence end in *ous*; those in which it has the higher valence end in *ic*, as ferr*ous* and ferr*ic* salts, arsen*ous* and arsen*ic* salts, etc.

The names of salts of all the hydracids end in *id*, as will be observed by referring to Table III; so also do the names of *all* other *binary* salts.

The terms *binary* and *ternary* salts designate those composed of only *two* or of *more* elements; thus, KCl, KCN, etc., are binary compounds, and $KClO_3$, KSCN, etc., are ternary compounds.

An oxid is a compound formed by the union of a metal or non-metal with oxygen. CaO, K_2O, MgO, CO_2, and N_2O_5.

An anhydrid is a compound left after removing from an acid all its replaceable hydrogen and enough oxygen to form water.

Examples. $H_2SO_4 - H_2O = SO_3$ = sulfuric anhydrid;
$2H_3PO_4 - 3H_2O = P_2O_5$ = phosphoric anhydrid;
$H_2CO_3 - H_2O = CO_2$ = carbonic anhydrid.

PART II.

IDENTIFICATION AND SEPARATION OF INORGANIC BASES AND ACIDS.

INTRODUCTORY.

19. **Qualitative Analysis** has for its object, the resolving of more or less complex substances into simpler ones, without reference to the proportions or quantities of the latter present.

By qualitative analysis usually we mean the examination of salts, i.e., combinations of *bases* and *acids*, the problem involved in such cases being the determination of the particular base and acid present in the given substance. Thus we examine a substance to determine not directly what *elements* are present, but what metals and what acidulous radicals—the latter usually being groups of elements. For example, in the analysis of barium sulfate we do not search for Ba, S, and O separately, but for barium as the base and SO_4 as the acidulous radical.

In some such cases as ammonium carbonate, $(NH_4)_2CO_3$, where neither the positive radical or base (NH_4) nor the negative or acidulous radical (CO_3) can exist in the free or uncombined state, we detect the former by the evolution of ammonia-gas (NH_3), and the latter by the expulsion of carbon dioxid (CO_2), from the substance. The word *analysis* is the true antithesis of the word *synthesis;* analysis meaning splitting up or breaking up of a substance, while synthesis means the building up of a compound from its elements.

Thus if we conduct an electric current into a solution of common salt, we split the compound into its components Na and Cl. This process is truly *analytical.* If we now bring sodium and chlorin together under suitable conditions, sodium chlorid will be formed in a *synthetical* way.

The word *analysis,* in chemistry, bears a wide meaning. It includes the manifold processes used by chemists in the identification of substances. Thus substances are often recognized by some characteristic appearance, like a particular crystalline form, when examined under a microscope, which operation is known as *microscopical* analysis. Often the presence of certain elements in a substance is determined by examining the light emitted when substances are strongly heated in a non-luminous flame before an optical apparatus known as a spectroscope, in which case the operation is known as *spectroscopic* analysis. Again, the substance may be examined in a polariscope as to its effect on light (much employed in oil and sugar analysis). In this last case the operation is called *polariscopic* analysis. The majority of analytical operations depend on some chemical change or reaction. When this change occurs on strongly heating a substance and observing its peculiar characteristics *in the dry way,* we call it a *dry reaction.* Again, when such a change occurs in the substance in the liquid form, by the action upon it of another liquid known as a *reagent,* we call it a *wet reaction.*

20. **Reagents,** or substances used to bring about chemical changes, may be in either the solid or the liquid state. For convenience in operation they are usually employed as liquids.*

Reagents are divided into three classes:

General Reagents, or group reagents, which under certain suitable conditions react with and precipitate a whole group or class of substances of similar character.

* Students should prepare their own reagents and not be kept in the dark as to their strength; it also gives them an idea of the delicacy of many of the reactions.

Separatory Reagents, by means of which the substance under examination is separated from other members of the same group; and

Confirmatory or Special Reagents, which are employed because they produce a certain peculiar characteristic reaction with a particular substance under examination, thus identifying it without any further doubt.

Reagents, says Prof. Newth, are "the tools with which the analyst works, and upon the intelligent and skilful use of them everything depends."

To the above a word on the *impurities in reagents* may be added. The student should constantly bear in mind that the substances he is testing for may be present in the reagents as impurities. In all such cases test the reagent directly, and by all means make sure of its purity; *it is imperative* for two reasons:

First: It precludes danger of serious errors, and

Second: It forms a habit of making blank tests with reagents and thus cultivating observation and logical reasoning powers.

In the course of qualitative analysis *wet reactions* are thought the more important.

When chemical reaction takes place between two or more substances in solution, and one of the products of the reaction is insoluble, it is thrown out of solution or *precipitated*, and is called a *precipitate* (abbr., ppt.).

In these operations the phenomenon of *precipitation* is taken advantage of.

In precipitation of a solution always add the reagent gradually, and only until no further precipitate forms. This can be determined by permitting the precipitate to settle, or, in case of light and flocculent precipitates which settle very slowly, by filtering a little of the liquid and adding to the filtrate a drop or two of the reagent.

In this way we guard against adding too much of the reagent,

which in many cases partly dissolves some of the precipitates —a very undesirable thing.

In washing a precipitate, persist until the wash-water will no longer give test for any substance known to be present in the filtrate, for if the precipitate is not thoroughly washed, the metal will be found present in succeeding groups, which will cause confusion and perhaps error in the analysis.

Guesswork will not do in these cases; you must be thorough, as on the complete precipitation of the substances and subsequent thorough washing of the precipitates the success of the analysis depends.

Separation of Groups.

If it were possible to precipitate by a separate reagent each individual metal out of a solution containing several different metallic salts, the analysis of such a solution would be a very simple matter.

Chemical analysis is, however, not so simple, for each reagent will precipitate more than one metal, and therefore in a solution containing a large number of metals the separation must be effected in groups.

Thus assuming that we have a solution containing twenty-four of the more common metals which we wish to analyze, the procedure must be as follows:

Hydrochloric acid is added to the solution in slight excess. This causes the precipitation of lead, silver, and mercury (if this is in the form of a mercurous salt), as chlorid. (*The Metals of Group I.*)

The hydrochloric acid should be added in sufficient quantity to precipitate all the lead, silver, and mercurous mercury (mercurosum) that may be present in the solution. To insure this, the precipitate is allowed to settle, and the clear liquid above it treated with a few drops more of hydrochloric acid. If this fails to produce a precipitate, the acid has been added in sufficient quantity. If, however, a precipitate is produced, more hydrochloric acid must be added. A large excess, however, is to be avoided.

N.B. Bismuth and *antimony* are precipitated by diluted hydrochloric acid, in the form of oxychlorids. Such a precipitate must not be mistaken for that of the metals of Group I.

Having precipitated the metals of Group I as above described, allow the precipitate to settle, and pass the supernatant liquid through a filter. This solution, which contains the remaining twenty-one metals, is treated with excess, of the Group II reagent, namely, *hydrogen sulfid* (H_2S). This causes the separation of seven more metals, namely, *mercury* in *mercuric salts* (mercuricum), *copper,* bismuth, cadmium, arsenic, antimony, and tin, in the form of sulfids. (*The metals of Group II.*)

These metals take up the sulfur from the hydrogen sulfid and form insoluble sulfids. In color the sulfids of mercury, copper, and bismuth so precipitated are black, cadmium and arsenic yellow, antimony orange, and tin brown or yellow.

The hydrogen sulfid is best used in the form of the pure gas, which should be allowed to bubble through the solution until the latter is thoroughly saturated. A saturated aqueous solution of the gas is sometimes used instead of the gas itself.

Having precipitated the metals of Group II, separate the precipitate by filtration. The filtrate now contains only fourteen metals. To this filtrate is added *ammonium chlorid,* about $\frac{1}{4}$ its volume, and *ammonium hydroxid* in sufficient quantity to render the solution alkaline, then a slight excess of *ammonium sulfid.* Another separation of seven metals will take place, namely, *iron, zinc, aluminum, manganese, chromium, cobalt,* and *nickel,* as *sulfids* except *aluminum* and *chromium,* which separate as *hydroxids.* (*The Metals of Group III.*)

The sulfur of the ammonium sulfid unites with the metals, iron, zinc, manganese cobalt, and nickel forming sulfids of these metals, but chromium and aluminum are precipitated as hydroxids. In color the precipitates produced with iron, cobalt, and nickel are black, with manganese flesh color, with zinc and aluminum white, and with chromium pale greenish.

Having added sufficient of the ammonium sulfid (the Group III reagent) to completely precipitate the metals, the

mixture is again filtered in order to separate the precipitate.

If now to the filtrate, in which only seven metals are left, an excess of *ammonium carbonate* solution be added, the metals *barium, calcium,* and *strontium* are precipitated in the form of carbonates (*Group IV*), leaving in solution *magnesium, potassium, sodium, ammonium,* and *lithium.* (*Group V.*)

From this solution the magnesium may be precipitated by adding *sodium phosphate.*

Since much ammonium has been added in the course of the analysis, a special test must be made for it in the original solution.

Each group of metals separated as above described is further separated into its component metals according to the charts, and each metal identified by characteristic tests.

These tests in most instances cannot be applied satisfactorily unless upon solutions of single metals.

THE SYSTEMATIC ANALYSIS OF A CHEMICAL SUBSTANCE, SIMPLE OR COMPOUND.

21. First, *if a solid:*

  a. Examine its general and physical characteristics, such as color, odor, reaction, structure (whether crystalline or amorphous), gravity, hardness, etc.

  b. Examine its solubility in water.

  c. Test its aqueous solution with litmus paper, both blue and red. If neither paper is affected, it is *neutral.*

  d. Heat a few centigrams of it with some NaOH or KOH in a test-tube, and note the odor. If NH_3 odor is noticed, it indicates the presence of an ammonium compound; if it turns black, a mercurosum salt (example, calomel) is present. Apply *special tests* for ammonium.

Second, *if a solid:*

(*a*) Heat about 20 centigrams of the solid in a dry test-tube held *horizontally* over a Bunsen-burner flame, and carefully note the effect.

By holding the mouth of the tube lower than the bottom all the moisture is permitted to run out, thus preventing its running back upon the over-heated portion of tube and breaking it.

(*b*) If the substance will *blacken or char* (due to the separation of carbon), it *indicates* the presence of an *organic substance,* like tartartes, citrates, sugar, alkaloid, gum, etc. It may here be added that a few organic substances, like the formates, oxalates, ferro- and ferricyanids, and cyanids, do not char.

(*c*) To remove the carbon thus obtained, let the test-tube cool off, add some strong H_2SO_4, and heat again. This treatment removes all the carbon from the tube.

Third, *if a liquid:*

(*a*) Test its reaction with both red and blue litmus, and observe whether it is alkaline (red paper turns blue with alkalies), acid (blue paper turns red with acids), or neutral (it does not affect the color of either paper.)

(*b*) Evaporate a portion of the liquid to dryness in a capsule, carefully noting the odor of the fumes (as NH_3, HCN, Cl, ClO, NO_2, etc., are thus detected).

(*c*) Heat the residue strongly. Charred or blackened residue indicates presence of organic matter.

(*d*) If the residue obtained above is not charred upon heating, it probably contains no organic matter, and is to be analyzed systematically and identified by chart 27 and the steps following.

FOURTH, *a solid or residue of a liquid can very frequently be identified by applying such preliminary examination as:*

(*a*) Heat test for solids, par. 22; for acids,		par.	76
(*b*) Flame test,	described in	"	63
(*c*) Sulfuric-acid test,	" "	"	23
(*d*) Borax-bead test,	" "	"	71
(*e*) Charcoal test,	" "	"	24
(*f*) Sodium-carbonate test,	" "	"	25
(*g*) Hydrochloric-acid test,	" "	"	26

Having applied all the above tests and not having identified the substance, examine it according to the table 27 for the identification of a *simple substance.*

By carefully applying the above-mentioned classes of tests nearly all the common metals and their salts may be readily detected.

In cases where the preliminary examination shows a number of metals present, separate them by carefully following *the tables* for the separation of the common metals.

HEAT TEST.

22. Heat a little of the substance as described in Second, above, and observe closely:

Observation.	Indication.
Substance blackens (carbonizes).	Presence of organic substance or of a metal forming a black oxid.
Moisture deposited.	Hydrate, or salt containing water of crystallization.
White sublimate formed in upper end of test-tube.	NH_4, Hg. (If accompanied by odor of garlic, it is As.)
White sublimate + odor of NH_3.	Ammonium benzoate.
Black sublimate + violet vapors.	Iodin or unstable iodid.
Reddish fumes.	Nitrites or nitrates.
Reddish-brown fumes, and drops which harden on cooling to yellow masses.	S or persulfids.
O_2 gas.	Inflames a glowing taper { Oxid, Chlorate, Permanganate

Observation.	Indication.
SO_2 gas (odor of burning sulfur).	Sulfate, sulfite, or sulfid.
NH_3 gas (its odor).	Ammonium salts, a cyanid, or nitrogenized organic substance.
CO gas (burning with a blue flame).	An oxalate.
CO_2 gas (causing turbidity in a drop of $Ba(OH)_2$, held on a rod above mouth of tube).	Carbonates, oxalates, and all carbonaceous matter.
Cl_2 gas evolved.	Hypochlorates.
Acetone evolved (burns).	Acetates.
Odor of valerianic acid.	Valerianates of zinc or soda.
" " phenol.	Carbolates, sulfocarbolates, or salicylates.
" " phosphorus (burning).	Hypophosphite.
" " burnt sugar.	Saccharose, lactose, glucose, tartrates.
" " burnt hair.	Alkaloid.

Sulfuric-acid Test.

23. Heat a portion (1 gm.) of the substance with a few drops of strong sulfuric acid, and observe:

Observation.	Indication.
Violent effervescence (no odor).	Carbonates or acid carbonates.
Effervescence + acid fumes; fumes white with ammonia.	Chlorid or nitrate.
Green or yellowish-green solution.	Chromium compound.
Red solution (at once).	Salicin.
Bluish solution forms.	Ferrocyanid.
Brown solution forms.	Tannin.
Chars to burnt sugar.	Saccharose or glucose.
Yellowish gas evolved (with crackling explosions).	Chlorate.
Violet fumes evolve.	Iodid.
Chars at first, with evolution of pungent acid fumes.	Citrate.
Reddish fumes evolved.	Nitrite, nitrate, or bromid.
Odor of burning sulfur.	Sulfite or thiosulfate.
Vapors evolved which, kindled, burn with a blue flame (CO).	Oxalates or ferri- and ferrocyanids.
Odor of HCN or vinegar.	Cyanid or acetate.

The Charcoal Test.

24. Heat a few centigrams of the substance on charcoal in the reducing (inner flame) with a blowpipe to red heat, and observe:

Observation.	Indication.
It decrepitates.	Chlorid or iodid.
It fuses readily and is absorbed by the charcoal.	Alkaline salts.
It deflagrates, igniting the charcoal.	A chlorate or nitrate.
A white mass, highly luminous, while heated, remains.	Alkaline earths of Al_2O_3, SiO_2, ZnO, Ba, Sr, Ca, Mg, or Sn.
Moisten the residue obtained above with solution $CO(NO_3)_2$, and heat strongly.	Blue = Al_2O_3 or phosphates and silicates.
If color is pale pink =	MgO.
" " " green =	ZnO, Sb.
A colored residue is left on charcoal.	Cu, Co, Fe, Ni, Mn, Cr.
An incrustation is formed on charcoal.	NH_4, Hg, Sb.
An incrustation with odor of garlic.	White = As.
An incrustation yellow while hot.	Greenish-white = Zn.
An incrustation.	Reddish brown = Cd.

Sodium-carbonate Test.

25. Mix about one gram of the substance with about 10 grams of sodium carbonate, and heat on charcoal in the reducing flame by means of a blowpipe, and observe:

Observation.	Indication.
Metallic bead, *malleable, with yellow incrustation.*	Lead.
Malleable metallic bead with no incrustation.	Silver.
Malleable bead *with white incrustation*	Tin
Brittle bead *with yellow incrustation.*	Bismuth.
Brittle bead, no incrustation.	Copper.
Brittle bead *with white incrustation.*	Antimony.
Grayish-black powder.	Iron, cobalt, nickel, or manganese.
Brown incrustation.	Cadmium.

The Hydrochloric-acid Test.

26. (1) Heat some of the substance in a test-tube with a little *dilute HCl*, and observe:

A gas is evolved:	Indication
CO_2 (apply lime-water test).	Carbonates.
H_2S, odor.	Sulfids.
SO_2, odor of burning sulfur.	Sulfites and thiosulfates.
Cl, odor; apply bleaching test.	$HClO_3$, or oxidizes like chromates or chlorates.
HCN (smell of bitter almonds).	Cyanids.

(2) Boil some of the substance in a test-tube with *concentrated HCl.* If not all dissolved, pour off the solution and divide it into five equal parts, to which apply the following tests:

To part 1 add KI, red ppt. soluble in excess.	Mercuricum.
" " 2 add KI, yellow ppt. insoluble in excess.	Lead.
" " 3 add NH_4OH; blue color develops.	Copper.
" " 4 add K_4FeCy_6; blue precipitate.	Iron.
Part 5. Evaporate to about one-fourth its original volume, pour a few drops of it into some cold water. White ppt. indicates either	Bismuth or antimony

27. TABLE FOR THE IDENTIFICATION

Group.	Reagent.	Result.	Indication.	Form.
I	To a portion of the original solution add *HCl*, drop by drop, until no further precipitate falls.	A curdy white precipitate, insoluble in excess of HCl.	Pb	
			Ag	
			Hg′	*ous*
II.	If no ppt. with HCl, or if the ppt. is soluble in excess of the reagent, pass H_2S through the acidified solution.	Black precipitate	Cu	
		" "	Hg″	*ic*
		" "	Pb	
		Dark-brown "	Bi	
		Yellow "	Cd	
		" "	As	
		Orange "	Sb	
		Brown "	Sn	*ous*
		Yellow "	Sn	*ic*
III.	If no precipitate with H_2S, add to fresh portion of original solution first NH_4Cl, then NH_4OH, and NH_4SH. Warm and filter.	Black precipitate	Fe	*ous*
		" "	Fe	*ic*
		" "	Co	
		" "	Ni	
		White "	Zn*	
		" "	Al*	

* If the ppt. in Group III is white in color and does not answer tests for Al or Zn, it may contain insoluble phosphates, metals, or oxalates, or all of these. Confirm by dissolving some of the original substance in conc. HNO_3 and pouring this into sol of ammonium molybdate.

OF THE METALS.

Confirmatory Tests, which should be applied to original solution.	Proof.
Ppt. soluble in boiling water. Add KI yellow preeipitate..... Test aiso by 2° and 3°, paragraph 30.	Pb
Ppt. insoluble in boiling H_2O. Add NH_4OH, the ppt. dissolves Test also by 1°, 2°, and 3°, paragraph 31.	Ag
Ppt. insoluble in boiling H_2O. Add NH_4OH, the white ppt turns black.. Test also by 2° and 3°, paragraph 32.	Hg′
Ppt. soluble, on heating, in excess of HCl..................	Sb or Bi
Ppt. soluble in KCy. Add NH_4OH = a light-blue ppt. soluble in excess.. Test also by 3° and 4°, paragraph 38.	Cu
Ppt. insoluble in $(NH_4)_2S$. Add KI = a red ppt. soluble in exeess Test also by 3°, paragragh 36.	Hg″
Ppt. insoluble in $(NH_4)_2S$ Add K_2CrO_4 = a yellow ppt......... Test also by 3° and 1°, paragraph 30.	Pb
Ppt. insoluble in $(NH_4)_2S$. Add KI = a greenish-brown ppt..... Test also by 3°, paragraph 37.	Bi
Ppt. insoluble in $(NH_4)_2S$, soluble in HNO_3. Add NH_4OH = a white ppt. soluble in excess.............................. Test also by 3° and 2°, paragraph 41.	Cd
Ppt. soluble in $(NH_4)_2S$, reprecipitated by HCl................ Test also by 3°, 4°, and 5°, paragraph 40.	As
Ppt. soluble in $(NH_4)_2S$, reprecipitated by HCl................ Test also by 3°, paragraph 42.	Sb
Ppt. soluble in $(NH_4)_2S$, reprecipitated yellow by HCl. Add NaOH = white ppt.; boil, ppt. insoluble.................... Test also by 3° and 2°, paragraph 44.	Sn″
Ppt. soluble in $(NH_4)_2S$, reprecipitated by HCl. Add NaOH = white ppt.; boil, ppt. dissolves.......................... Test also by 2°, paragraph 43.	Sn^{IV}
Ppt. soluble in HCl. Add K_4FeCy_6 = white ppt., rapidly turning blue.. Test also by 2° and 3°, paragraph 49.	Fe″
Ppt. soluble in HCl. Add K_4FeCy_6 = heavy-blue ppt. insoluble in acids.. Test also by 3°, 4°, and 2°, paragraph 48.	Fe‴
Ppt. insoluble in dil. HCl. Add NH_4OH = a blue ppt. soluble in excess to a brown solution.............................. Test also by 2°, paragraph 50.	Co
Ppt. almost insoluble in dil. HCl. Add K_3FeCy_6 = a yellow ppt. Test also by 3° and 2°, paragraph 51.	Ni
Ppt. soluble in HCl. Add K_4FeCy_6 = white ppt.............. Test also by 2°, paragraph 52.	Zn
Ppt. soluble in HCl. Add KOH = white ppt. soluble in exeess, reprecipitated by NH_4Cl.................................. Test also by 3°, paragraph 53.	Al

Yellow precipitate or coloration on boiling indicates insoluble phosphate; in which case treat as described later on.

TABLE FOR THE IDENTIFICATION

Group.	Reagent.	Result.	Indication.	Form.
III. (*con'd*)		Flesh-colored precipitate	Mn	
		Green precipitate	Cr	
IV.	If reagents of Group III give no precipitate, add $(NH_4)_2CO_3$. Warm and filter.	White precipitate	Ba	
		" "	Sr	
		" "	Ca	
V.	If reagent of Group IV gives no precipitate, add Na_2HPO_4.	White precipitate	Mg	

If reagent of Group IV gives no ppt.,

28. CHART FOR THE SEPARATION OF THE METALS.

Group I.

Group Reagent: Dilute hydrochloric acid.

To a portion of the original cold solution add some *dilute* HCl. A white *curdy* precipitate indicates:

1.* Pb, Ag, Hg′ (*ous*), (Sb, Bi).

3. Insoluble in excess.
Pb, Ag, Hg.
Wash with cold H_2O, then pour boiling H_2O over precipitate.

2. Soluble in excess.
Sb, Bi.
These are confirmed in the next group.

5. Insoluble.
Ag, Hg′.
Pour over precipitate some warm NH_4OH.

4. Soluble.
Pb.
Confirm by adding
H_2SO_4 white ppt. = Pb.
KI yellow " = Pb.
K_2CrO_4 orange-yel. " = Pb.

7. Insoluble.
Hg.
Pour over this black ppt. on filter a few drops of aqua regia, dilute with H_2O, add some $SnCl_2$: grayish or blackish ppt. = Hg.

6. Soluble.
Ag.
Confirm by adding HNO_3 in excess: white ppt. = Ag.

* The numbers refer to numbers of the *Notes*.

OF THE METALS—*Continued.*

Confirmatory Tests, which should be applied to original solution.	Proof.
Ppt. soluble in dil. HCl. Add KOH = white ppt.; shake; turns brown .... Test also by 2°, 3°, and 4°, paragraph 54.	Mn
Ppt. soluble in dil. HCl. Add KOH = green ppt. soluble in excess, reprecipitated on boiling....... Test also by 2° and 3°, paragraph 55.	Cr
Ppt. soluble in HCl. Add K_2CrO_4 = yellow precipitate....... Test also by 3° and 4°, paragraph 59.	Ba
Ppt. soluble in HNO_3. Add K_2CrO_4 = no ppt. Add sol. $CaSO_4$, shake = white ppt. .... Test also by 3°, paragraph 60.	Sr
Ppt. soluble in acids. Add K_2CrO_4 = no ppt. Add sol. $CaSO_4$ shake = no ppt. Add $(NH_4)_2CrO_4$ = white ppt. .... Test also by 3°, paragraph 61.	Ca
Add $(NH_4)_2CO_3$ and boil = white ppt.	Mg

test for K, Na, and NH_4, as per paragraph 62.

29. Notes on Group I.

(1) On the addition of HCl the following chlorids are formed: lead chlorid ($PbCl_2$), silver chlorid (AgCl), and mercurous chlorid (HgCl). These being insoluble are precipitated together with the oxychlorids of antimony (SbOCl) and bismuth (BiOCl). The first three are insoluble in weak acids; the remaining two are soluble in excess of weak acids and water, therefore remain in the filtrate. Lead chlorid is slightly soluble in water, and when present in mere traces only, it passes into Group II, where it precipitates as sulfid.

It is advisable to use dilute HCl for two reasons:

(*a*) Strong HCl precipitates various other salts from strong solutions.

(*b*) AgCl and HgCl are to some extent soluble in strong HCl; traces of these might therefore be overlooked.

(2) The BiOCl and SbOCl are soluble in HCl, and hence pass over into Group II.

(3) When boiling H_2O is poured over the precipitate, the lead chlorid being soluble passes through the filter and deposits on cooling.

The presence of lead in the filtrate may be proven by dividing it into three portions, and tests applied to each portion. See par. 30.

(5) When solution of NH_4OH is poured over the precipitate left on filter, the AgCl dissolves, forming argentic amin, $AgCl(NH_3)_2$.

The insoluble ppt. left on the filter is the black mercurous amin, NH_2Hg_2Cl, which is rather unstable and yields some metallic mercury by decomposition.

(6) The addition of the HNO_3 in the confirmatory test neutralizes the ammonia, and the AgCl is thrown down as a white curdy precipitate.

(7) The Hg″ may also be proved by mixing some of the black precipitate with dry Na_2CO_3 and heating in a tube, when metallic globules or a mirror of mercury will be formed.

When aqua regia is poured over the precipitate it forms mercuric chlorid ($HgCl_2$), which is reduced by stannous chlorid ($SnCl_2$) to grayish-white mercurous chlorid (Hg_2Cl_2) or blackish-gray metallic mercury (Hg).

SPECIAL TESTS FOR METALS OF GROUP I.

(Chlorid Group.)

Each of these tests should be applied to a fresh portion of the original solution.

30. **Lead.**

Precipitated by HCl = a white crystalline precipitate of $PbCl_2$ soluble in hot water:

$$Pb(NO_3)_2 + 2HCl = \underbrace{PbCl_2}_{\text{Plumbic Chlorid.}} + 2HNO_3.$$

1°. *The Iodid Test:* KI gives a crystalline yellow ppt., PbI_2, soluble in hot water:

$$Pb(NO_3)_2 + 2KI = \underbrace{PbI_2}_{\text{Lead Iodid.}} + 2KNO_3.$$

2°. *The Chromate Test:* K_2CrO_4 gives a bright-yellow ppt., $PbCrO_4$, soluble in NaOH:

$$Pb(NO_3)_2 + K_2CrO_4 = \underbrace{PbCrO_4}_{\text{Lead Chromate.}} + 2KNO_3.$$

3°. *The Sulfuric Acid Test:* H_2SO_4 gives a white ppt., $PbSO_4$, soluble in NaOH:

$$Pb(NO_3)_2 + H_2SO_4 = \underbrace{PbSO_4}_{\text{Lead Sulfate.}} + 2HNO_3.$$

31. Silver.

Precipitated by HCl = a white ppt. AgCl, soluble in NH_4OH; reprecipitated by HNO_3:

$$AgNO_3 + HCl = \underbrace{AgCl}_{\text{Silver Chlorid}} + HNO_3.$$

1° *Ammonia Test.*—NH_4OH = a brownish-gray ppt., Ag_2O, soluble in excess:

$$2AgNO_3 + 2NH_4OH = \underbrace{Ag_2O}_{\text{Silver Oxid.}} + 2NH_4NO_3 + H_2O.$$

2° *Chromate Test.*—K_2CrO_4 = a brick-red ppt., Ag_2CrO_4, soluble in NH_4OH:

$$2AgNO_3 + K_2CrO_4 = \underbrace{Ag_2CrO_4}_{\text{Silver Chromate.}} + 2KNO_3.$$

3° *Iodid Test.*—KI = a pale-yellow ppt., AgI, insoluble in NH_4OH:

$$AgNO_3 + KI = \underbrace{AgI}_{\text{Silver Iodid.}} + KNO_3.$$

32. Mercurous Salts.

Precipitated by HCl = a white ppt., Hg_2Cl_2, blackened by NH_4OH:

$$Hg_2(NO_3)_2 + 2HCl = \underbrace{Hg_2Cl_2}_{\text{Mercurous Chlorid.}} + 2HNO_3.$$

1° *Iodid Test.*—KI = a greenish-yellow ppt. of Hg_2I_2:

$$Hg_2(NO_3)_2 + 2KI = \underbrace{Hg_2I_2}_{\text{Mercurous Iodid.}} + 2KNO_3$$

2° *Ammonia Test.*—NH_4OH = a black ppt. insoluble in excess:

$$Hg_2(NO_3)_2 + 2NH_4OH = \underbrace{NH_2Hg_2NO_3}_{\text{Mercurous Ammonium Nitrate.}} + NH_4NO_3 + 2H_2O.$$

33. CHART FOR SEPARATION OF GROUP II.

Pass H_2S gas into the hot filtrate of Group I until it smells strongly of the gas after shaking. Heat to boiling, pass some more H_2S into the solution, allow the precipitate to subside, filter, wash the precipitate with boiling-hot water until free from acid. Test a small portion of the filtrate, diluted with water, by passing more H_2S through it, to see if the precipitation is complete. The precipitate may contain

Cu, Pb, Hg, Bi, Cd, As, Sb, Sn.

Wash with boiling-hot water, add a few drops of NH_4OH and excess of $(NH_4)_2S$.

11. Insoluble.
Cu, Pb, Hg, Bi, Cd.
Wash, pour dil. boiling HNO_3 over the filter.

12. Insoluble.
Hg.
Dissolve in aqua regia by aid of heat. Evaporate to dryness, dilute with H_2O, and add KI: red ppt. = Hg.

13. Soluble.
Cu, Pb, Bi, Cd.
Add dil. H_2SO_4, boil well, filter.

14. Insoluble.
Pb.
Dissolve the ppt. in $NH_4C_2H_3O_2$, add KI: yel. ppt. = Pb. Add $K_2C_2O_4$: orange ppt. = Pb.

15. Soluble.
Cu, Bi, Cd.
Dilute with H_2O, add excess of NH_4OH and filter.

16. Insoluble.
Bi.
Wash, dissolve in small quantity of warm dil. HCl, evaporate to a low bulk, and pour into a large volume of water: white ppt. = Bi.

17. Soluble.
Cu, Cd.
A blue solution indicates Cu. Add a little HNO_3. Divide into two portions.

Add NH_4OH: blue = Cu.

Add NH_4OH, acidulate with HCl, pass H_2S: yel. ppt. = Cd.

8. Soluble.
As, Sb, Sn.
Add dil. HCl, filter and wash and dissolve in strong HCl, boil gently, filter.

9. Insoluble.
As and S.
Apply Marsh's test.

10. Soluble.
Sn and Sb.
Boil with copper turnings and divide into two portions.

Add $HgCl_2$ white or grayish ppt. = Sn.

Confirm presence of Sb by Marsh's test.

34. Observations on Group II.

The separation of the members of this group requires very careful manipulation to insure success.

The precipitate may contain any or all of the following metals possessing characteristic colors, thus: Black or brownish black: CuS, PbS, HgS, Bi_2S_3, SnS. Yellow: CdS, As_2S_3, As_2S_5, SnS_2. Orange: Sb_2S_3, Sb_2S_5. When H_2S is first passed into solutions containing lead and mercuric mercury they give colored precipitates due to formation of double salts, thus: $HgCl_2Hg$. At first it is white, then it turns red, brown, and finally black under the continuous action of H_2S, owing to the formation of HgS. Lead salts under like conditions give red precipitates gradually changing to brown, then to black, owing the conversion to PbS.

In addition to the above-mentioned sulfids of this group a white precipitate of sulfur is formed, especially if the original solution is very acid or when it contains a ferric salt, chromic or nitric acid, or a chlorate. These substances being strong oxidizing agents will be reduced by the H_2S, precipitating sulfur, which is easily distinguished from CdS and As_2S_3 by its lighter color and density.

Ferric salts will be reduced to ferrous salts:

$$Fe_2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S.$$

Chromic acid will be reduced to chromic chlorid:

$$2H_2CrO_4 + 3H_2S + 6HCl = Cr_2Cl_6 + S_3 + 8H_2O$$

Nitric acid will be reduced to nitric oxid:

$$2HNO_3 + 3H_2S = 2NO + S_3 + 4H_2O.$$

As said above, it is almost useless to pass H_2S into very acid solutions, especially those containing HNO_3 or aqua regia. If these acids have been used in dissolving the original, the solution so formed should be first evaporated to dryness

the residue dissolved in a little water with the aid of a few drops of HCl, before passing H_2S into it. It is, however, *essential* that the solution be slightly *acid;* this is necessary to prevent the precipitation of Zn, Co, and Ni.

Complete precipitation of the second group often seems tedious, but it should under no circumstances be scamped, if accurate and definite results are to be obtained.

To attain this end it is necessary, first, to pass a sufficient quantity of H_2S; second, to test a portion of the solution by filtration, dilution, and repeated precipitation until the saturation be complete.

The metals precipitate much more quickly from a hot than a cold solution, especially arsenicum; its yellow precipitate forms very slowly, thus: $2H_3AsO_4+5H_2S=As_2S_5+8H_2O$; and to facilitate its precipitation the solution should be well heated from time to time.

Besides the above reason, the sulfids thus precipitated from hot, weakly acid solutions and allowed to stand may be filtered much more easily, for they exhibit to a marked degree the property of becoming "colloidal" and consequently passing through the filter-paper upon washing. If water saturated with H_2S or very dilute acetic acid be used for washing the precipitate, this tendency is checked.

35. NOTES ON GROUP II.

8. The object of adding a little NH_4OH before the addition of $(NH_4)_2S$ is to neutralize the acid present, thus preventing the precipitation of sulfur. The precipitate should be *digested, not boiled:* boiling precipitates some As, Sb, Sn. These sulfids unite with the $(NH_4)_2S$, with the formation of salts of the sulfo-acids, thus:

$$As_2S_3+3(NH_4)_2S_x=2(NH_4)_3AsS_3;$$
$$Sb_2S_3+3(NH_4)_2S_x=2(NH_4)_3SbS_3;$$
$$SnS+(NH_4)_2S_x=(NH_4)_2SnS_2.$$

The $(NH_4)_2S$ solution should be warmed with diluted HCl (the strong acid dissolves Sb_2S_3). This reprecipitates all the sulfids which must be filtered off and washed from the soluble ammonium compounds. This reprecipitation is due to the instability of the free acids (formed by the HCl) corresponding to the sulfo-acid ammonium compounds above mentioned. On adding strong HCl and boiling, Sb and Sn dissolve as chlorids, while the yellow arsenic sulfid remains undissolved. The boiling is necessary to drive off the H_2S.

9. The black spot formed in Marsh's test is soluble in solutions of chlorinated soda or calcium. If part of the solution is treated with CS_2, and this solution allowed to evaporate spontaneously, free S is separated.

10. The acid solution on being boiled with metallic copper (preferably turnings) reduces the stannic chlorid to stannous according to the reaction $SnCl_4 + Cu = SnCl_2 + CuCl_2$. The $SnCl_2$ reduces mercuric chlorid ($HgCl_2$) to the mercurous chlorid (Hg_2Cl_2) or gray metallic Hg, according to the quantity of $SnCl_2$ present.

11. The precipitate should be well washed to insure absence of the metals of Group III, as the $(NH_4)_2S$ will precipitate the metals of the aluminum and iron groups.

12. Mercuric sulfid (HgS) is insoluble in boiling dilute HNO_3, but, owing to the presence of other sulfids, the treatment with HNO_3 will cause evolution of H_2S and formation of nitrates and free sulfur, thus:

$$3H_2S + 2HNO_3 = S_3 + 2NO + 4H_2O.$$

The free sulfur thus formed occludes a portion of the sulfids other than HgS, and protects them from action of the HNO_3. Therefore the black residue thus formed which is insoluble in HNO_3 should always be further tested before rejecting it.

HgS dissolved in aqua regia forms $HgCl_2$; this should be evaporated to dryness to get rid of the chlorin, which would liberate free iodin on the addition of KI.

The KI should be added drop by drop, as the red mercuric iodid (HgI_2) thus formed is soluble in excess of the reagent. Hg may further be identified by adding a few drops of solution stannous chlorid ($SnCl_2$), when a grayish-white precipitate will form. Or, the precipitated HgS may be fused with potassium cyanid (KCy) and sodium carbonate (Na_2CO_3) in a dry tube, when Hg will sublime a little above the fused mass.

13. The sulfids of Cu, Pb, Bi, Cd, dissolve in the nitric acid, forming corresponding nitrates. Evaporate this nitrate solution to about one-fourth the original bulk and add sufficient dilute H_2SO_4 to displace the nitric acid and form corresponding sulfates. Continue evaporation until white H_2SO_4 fumes appear. This is a sign that all the HNO_3 is dissipated, which is important for the reason that lead nitrate might remain in solution and interfere in the detection of cadmium.

Cool the solution of sulfates, and dilute with water. The sulfates of bismuth, copper, and cadmium go in solution and may be readily filtered off from the insoluble $PbSO_4$.

14. Lead sulfate dissolves readily in ammonium acetate, forming a double salt. Divide this solution into two portions; to one add KI; lead iodid will form: $PbSO_4 + 2KI = PbI_2 + K_2SO_4$. To the other portion add K_2CrO_4; lead chromate will form according to the reaction $PbSO_4 + K_2CrO_4 = PbCrO_4 + K_2SO_4$. Lead iodid forms a yellow, and the chromate an orange-colored, precipitate. Either of the reagents may be applied directly to the $PbSO_4$ on the filter.

15. The filtrate must be slightly diluted with water before addition of NH_4OH. The Cu and Cd dissolve in the ammonium hydroxid to form soluble ammonium compounds, while the Bi is precipitated as hydroxid, $Bi(OH)_3$.

16. Filter off the $Bi(OH)_3$ and dissolve it on the filter by pouring warm dilute HCl over the precipitate, returning the filtrate until all the precipitate has passed into solution. The solution contains $BiCl_3$, and on evaporating it to a small bulk to free it from excess of the HCl and pouring it into a large

volume of water, a white, cloudy precipitate of bismuth oxychlorid ($BiOCl$) is produced. The evaporation to a small bulk above directed is for the purpose of increasing the delicacy of the test, as the less HCl used for dissolving the $Bi(OH)_3$ the more positive does this reaction become.

17. If the solution be of a blue color, it indicates the presence of copper, the color being due to the formation of a new compound, ammonio-sulfate of copper. Add to this solution a few drops of HNO_3, and divide into two portions, *a* and *b*. To portion *a* add NH_4OH; a blue color = copper. To portion *b* add NH_4OH, acidulate with HCl, and pass H_2S through the solution; a yellow precipitate indicates cadmium sulfid, CdS.

SPECIAL TESTS FOR METALS OF GROUP II.

(ACID SULFID GROUP.)

Each test to be made upon a fresh portion of the original solution.

36. Mercuricum.

Precipitated from acid solution by H_2S = a reddish-black ppt. of HgS, insoluble in HNO_3:

$$HgCl_2 + H_2S = \underbrace{HgS}_{\text{Mercuric Sulfid.}} + 2HCl.$$

1° *Sodium Hydroxid Test.*—$NaOH$ = a yellow ppt. of mercuric oxid, HgO, insoluble in excess:

$$HgCl_2 + 2NaOH = \underbrace{HgO}_{\text{Mercuric Oxid.}} + 2NaCl + H_2O.$$

2° *Potassium Iodid Test.*—KI = a red ppt. of mercuric iodid, HgI_2, soluble in excess of KI and $HgCl_2$:

$$HgCl_2 + 2KI = \underbrace{HgI_2}_{\text{Mercuric Iodid.}} + 2KCl.$$

3° *Ammonia Test.*—NH_4OH = a white ppt. of mercuric ammonium chlorid, NH_2HgCl:

$$HgCl_2 + 2NH_4OH = \underbrace{NH_2HgCl}_{\text{Mercuric Ammonium Chlorid.}} + NH_4Cl + 2H_2O.$$

37. **Bismuth.**

1° H_2S in acid solution = a brown ppt. of Bi_2S_3, insoluble in $(NH_4)_2S$:

$$2Bi(NO_3)_3 + 3H_2S = \underbrace{Bi_2S_3}_{\text{Bismuthic Sulfid.}} + 6HNO_3.$$

2° *Potassium Iodid Test.*—KI = a greenish-brown ppt. of BiI_3, soluble in excess:

$$Bi(NO_3)_3 + 3KI = \underbrace{BiI_3}_{\text{Bismuth Iodid.}} + 3KNO_3.$$

3° *Chromate Test.*—K_2CrO_4 = a yellow ppt. of $Bi_2(CrO_4)_3$:

$$2Bi(NO_3)_3 + K_2CrO_4 = \underbrace{Bi_2(CrO_4)_3}_{\text{Bismuth Chromate.}} + 6KNO_3.$$

38. **Copper.**

Precipitated from acid solutions by H_2S = a brownish-black ppt. of CuS, soluble in KCy:

$$CuSO_4 + H_2S = \underbrace{CuS}_{\text{Copper Sulfid.}} + H_2SO_4.$$

1° *Ammonia Test.*—NH_4OH = a blue ppt. soluble in excess to a dark-blue liquid:

$$CuSO_4 + 2NH_4OH = Cu(OH)_2 + (NH_4)_2SO_4$$

and

$$CuSO_4 + 4NH_4OH = \underbrace{Cu(NH_4)_2(NH_2)_2SO_4}_{\text{Ammonio-cupric Sulfate.}} + 4H_2O.$$

2° *Sodium Hydroxid Test.*—NaOH = a blue ppt., becoming black, CuO, on boiling.

$$CuSO_4 + 2NaOH = \underbrace{Cu(OH)_2}_{\text{Copper Hydroxid.}} + Na_2SO_4$$

and

$$Cu(OH)_2 + \text{heat} = CuO + H_2O.$$

3° *Ferrocyanid Test.*—K_4FeCy_6 = a brown ppt. of Cu_2FeCy_6, insoluble in dilute acids:

$$2CuSO_4 + K_4FeCy_6 = \underbrace{Cu_2FeCy_6}_{\text{Copper Ferrocyanid.}} + 2K_2SO_4.$$

4° *Borax-bead Test.*—In O flame = green; blue when cold.

39. **Arsenic.**

Precipitated from acid solutions by H_2S = a yellow ppt. of As_2S_3:

$$As_2O_5 + 5H_2S = \underbrace{As_2S_3}_{\substack{\text{Arsenous}\\ \text{Sulfid.}}} + 5H_2O + S_2.$$

Upon boiling and passing an excess of H_2S through the solution, As_2S_5 is pptd.

1° *Ammonio-Silver-nitrate Test.*—$AgNO_3$ in NH_4OH solution = a reddish-brown ppt. of Ag_3AsO_4.

This is the differentiating test from arsenosum, which compare.

40. **Arsenous.**

Precipitated from acid solutions by H_2S = a yellow ppt. of As_2S_3, soluble in $(NH_4)_2S$, and reprecipitated by HCl:

$$2As_2O_3 + 6H_2O = 4H_3AsO_3$$

and

$$4H_3AsO_3 + 6H_2S = \underbrace{2As_2S_3}_{\text{Arsenous Sulfid.}} + 12H_2O.$$

1° *Copper-sulphate Test.*—In neutral solutions $CuSO_4$ = a pale-green ppt. of $CuHAsO_3$ (Scheele's green), soluble in NH_4OH:

$$H_3AsO_3 + CuSO_4 + 2NH_4OH = \underbrace{CuHAsO_3}_{\text{Copper Arsenite.}} + (NH_4)_2SO_4 + 2H_2O.$$

2° *Ammonio-Silver-nitrate Test.*—$AgNO_3$ in NH_4OH solution = yellow ppt. Ag_3AsO_3 (silver arsenite):

$$H_3AsO_3 + 3AgNO_3 = Ag_3AsO_3 + 3HNO_3.$$

3° *Charcoal Test.*—Heated on charcoal, arsenic gives a white incrustation and a garlicky odor.

4° Apply both Marsh's and Fleitmann's tests.

Marsh's Arsenic Test.—Generate hydrogen with dilute H_2SO_4 and metallic zinc in a bottle furnished with a jet and funnel-tube. After the gas has been given off in sufficient quantity to expel all the air contained in the bottle, the gas is ignited and the arsenical solution introduced through the funnel-tube.

The yellow hydrogen flame is at once changed to a bluish flame characteristic of arsenic, and which emits a garlicky odor. If a piece of cold porcelain is held in this flame, a brownish-black spot of metallic arsenic is deposited upon it. (This is called an arsenic-spot.) The zinc and sulfuric acid used for generating the hydrogen must both be free from arsenic.

Marsh's test is based on the formation of arsine gas, AsH_3, the product of the action of nascent hydrogen upon arsenic in an acid medium:

$$6Zn + 6H_2SO_4 + As_2O_3 = 2AsH_3 + 6ZnSO_4 + 3H_2O.$$

Marsh's test, further, is used to differentiate between arsenic and antimony in a solution; for instance, antimony produces the same kind of spot as arsenic, but the arsenic spots dissolve readily when treated with a few drops of a hypochlorite or euchlorin solution, while the antimony spots are not affected.

5° *Fleitmann's Test for Arsenic.*—A fragment of metallic zinc or aluminum is placed in a test-tube with some KOH solution, and a small quantity of the arsenical solution is added.

Heat the mixture and place over the mouth of the tube a cap of paper moistened with a solution of $AgNO_3$. The arsine which is evolved acts upon the silver nitrate, reducing it to metallic silver, which is shown by the development of a dark stain on the paper.

The advantage of this test lies in the fact that stibine is not evolved in alkaline solutions as in the case of Marsh's test, and hence only arsenic reacts in the manner described:

$$Zn + 2KOH = \underbrace{K_2ZnO_2}_{\text{Potassium Zincate.}} + H_2;$$

$$H_3AsO_3 + 3H_2 = \underbrace{AsH_3}_{\text{Arsine.}} + 3H_2O;$$

$$AsH_3 + 6AgNO_3 + 3H_2O = \underbrace{3Ag_2}_{\text{Metallic Silver.}} + H_3AsO_3 + 6HNO_3.$$

41. Cadmium.

Precipitated from acid solution by H_2S = yellow ppt. CdS insoluble in $(NH_4)_2S$ but soluble in HNO_3. This ppt. will form

in the presence of potassium cyanid (distinction from copper):

$$CdCl_2 + H_2S = \underbrace{CdS}_{\text{Cadmium Sulfid.}} + 2HCl.$$

1° *Ammonia Test.*—NH_4OH = a white ppt. of $Cd(OH)_2$, soluble in excess:

$$CdCl_2 + 2NH_4OH = \underbrace{Cd(OH)_2}_{\text{Cadmium Hydroxid.}} + 2NH_4Cl.$$

2° *Sodium-hydroxid Test.*—$NaOH$ = a white ppt. of $Cd(OH)_2$, insoluble in excess:

$$CdCl_2 + 2NaOH = Cd(OH)_2 + 2NaCl.$$

3° Apply *sodium-carbonate test,* paragraph 25. A brown coating of CdO; no metallic bead.

42. Antimony.

Precipitated from acid solutions by H_2S = an orange ppt. of Sb_2S_3, soluble in $(NH_4)_2S$, and reprecipitated by HCl. The ppt. is not soluble in $(NH_4)_2CO_3$ solution (distinction from arsenic):

$$2SbCl_3 + 3H_2S = \underbrace{Sb_2S_3}_{\text{Antimonic Sulfid.}} + 6HCl.$$

1° *Copper Test.*—Metallic copper in acid solutions of antimony receives a grayish deposit of antimony; when this is heated in a test-tube a white ring of Sb_2O_3 forms in the tube, near the copper:

$$Cu_5 + Sb_4 + 3O_2 = \underbrace{Cu_5}_{\text{Metallic Copper.}} + 2Sb_2O_3.$$

2° *Water Test.*—Slightly acid solutions of $SbCl_3$ poured in water = a white ppt. of $(SbOCl)_2 + Sb_2O_3$, soluble in tartaric acid:

$$4SbCl_3 + 5H_2O = \underbrace{(SbOCl)_2 + Sb_2O_3}_{\text{Powder of Algaroth.}} + 10HCl.$$

3° Apply *Marsh's test.*

43. Stannic Salts.

H_2S precipitates from acid solutions SnS_2 = a yellow ppt. slowly soluble in $(NH_4)_2S$, and reprecipitated by HCl:

$$SnCl_4 + 2H_2S = \underbrace{SnS_2}_{\substack{\text{Stannic}\\\text{Sulfid.}}} + 4HCl:$$

1° *Sodium-hydroxid Test.*—NaOH = white ppt. $Sn(OH)_4$:

$$SnCl_4 + 4NaOH = \underbrace{Sn(OH)_4}_{\text{Stannic Hydroxid.}} + 4NaCl.$$

2° *Molybdenum Test.*—$(NH_4)_2MoO_4$ = no blue coloration (distinction from stannous).

44. Stannous Salts.

Precipitated by H_2S from acid solution as SnS = a brown ppt. slowly soluble in $(NH_4)_2S$; reprecipitated by HCl = a yellow ppt. of SnS_2:

$$SnCl_2 + H_2S = SnS + 2HCl;$$

1° *Sodium-hydroxid Test.*—NaOH = a white ppt. of $Sn(OH)_2$, soluble in excess of reagent:

$$SnCl_2 + 2NaOH = Sn(OH)_2 + 2NaCl;$$

$$Sn(OH)_2 + 2NaOH = \underbrace{Na_2SnO_2}_{\substack{\text{Sodium}\\\text{Stannite.}}} + 2H_2O.$$

2° *Mercuric Test.*—$HgCl_2$ produces in solutions of stannous salts a white ppt. of Hg_2Cl_2 which darkens on boiling, being reduced to Hg:

$$SnCl_2 + HgCl_2 = SnCl_4 + Hg.$$

3° *Molybdenum Test.*—$(NH_4)_2MoO_4$ = a blue ppt. (distinction from stannic tin).

45. CHART FOR THE SEPARATION OF GROUP III.

18. Evaporate filtrate from Group II, or if Groups I and II were found to be absent, a separate portion of the original solution is taken. As the filtrate plus the washings from Group II are quite voluminous, it is desirable to carry the evaporation down to one-sixth or less of the original bulk.

Here also account must be taken of the fact whether or not organic substances like citric, tartaric, or malic acid, glycerin, etc., be present; also the presence of phosphates and oxalates should be determined, as these interfere.

If iron has been detected in the preliminary tests, add a few drops of strong HNO_3 and boil well, next add a little solution of NH_4Cl and excess of NH_4OH, boil and filter.

19. Precipitate.
Fe, Al, Cr, Mn (traces).
Insoluble phosphates and oxalates. (Dissolve some original substance in strong HNO_3, boil, pour into some solution of ammonium molybdate, and boil. Yellow coloration or precipitate indicates insoluble phosphates.) See paragraph 81.

Fuse ppt. with 4 times its weight of a mixture of Na_2CO_3 and KNO_3 in a crucible or on a platinum foil, treat mass with boiling-hot water, and filter

20. Insoluble.
Fe.
Pour HCl over the ppt. on filter and divide the filtrate into two portions: to (1) add K_4FeCy_6= blue ppt. = Fe; to (2) add KCyS= red color = Fe.

21. Soluble.
Al, Cr.
Divide this sol. into two portions and test for Al and Cr.

22. Acidify with $HC_2H_3O_2$; to one portion add excess of $AgNO_3$ = red ppt. = Cr; to another portion add some sol. $Pb(C_2H_3O_2)_2$ = yellow ppt. = Cr.

23. Acidify with HCl, add a large excess of NH_4OH and shake well; white ppt. = Al.

24. Filtrate.
Zn, Co, Ni, Mn.
Add $(NH_4)_2S$: all the sulfids are ppt'd Dissolve ppt. in HCl, add excess of NH_4OH, acidify with $HC_2H_3O_2$, pass H_2S through the solution, and filter

25. Precipitate.
If white = Zn. If black = CO or Ni. Dissolve in HCl; add sol. KCy and solution of chlorinated soda, boil, and filter.

26 Precipitate..
Ni.

27. Solution.
Co.

Confirm both by borax bead.

28. Solution.
Mn.
Fuse with a fusing mixture; green residue = Mn.

46. Observations on Group III.

The object of evaporating the filtrate from Group II is to dissipate the H_2S and thus prevent the formation of $(NH_4)_2S$, which in turn would precipitate the iron, cobalt, and nickel, etc.

Attention here is called to organic substances mentioned in No. 18, paragraph 45.

The precipitation of iron, aluminum, and chromium as hydroxids can only be accomplished in the absence of organic acids and other organic substances, like sugar or glycerin, containing several of the hydroxyl groups. Therefore, if these be detected in the preliminary tests, evaporate the H_2S filtrate to dryness, heat the residue with a few drops of strong HNO_3 (thus decomposing organic substances), dissolve the residue in HCl, and proceed in the usual way.

Should organic substances be absent, boil the solution with HNO_3 to oxidize the ferrous salts to the ferric state (thus insuring the complete precipitation of iron by ammonia). Excess of HNO_3 should be avoided.

The NH_4OH (which should be added until the solution smells strongly of NH_3) precipitates $Fe_2(OH)_6$, $Al_2(OH)_6$, and $Cr_2(OH)_6$, with a trace of manganese. Zinc, manganese, cobalt, and nickel, which are also precipitated, form soluble hydroxids which dissolve in the excess of NH_4OH, and are found in the filtrate.

Although the manganese is soluble in the excess of NH_4OH, during the heating and subsequent filtration employed in the separation of the Al and Cr, it absorbs oxygen, and from manganous becomes oxidized to mangano-manganic oxid (Mn_2O_3), which, being insoluble in NH_4OH, is precipitated together with the Fe, Al, and Cr. The object of adding NH_4Cl before the group reagent NH_4OH is to prevent the precipitation of $Mg(OH)_2$, which forms a soluble double compound, $MgCl_2.2NH_4Cl$. The solution of NH_4Cl also facilitates the

complete solution of Co, Ni, Zn, and Mn in the excess of NH_4OH. To completely precipitate the Al and Cr, the mixture must be boiled.

47. Notes on Group III.

19. When dried and fused the hydroxids lose water and are converted into oxids, Fe_2O_3, Al_2O_3, and Cr_2O_3. When treated with water and filtered, the Fe_2O_3 remains as an insoluble reddish-brown powder on the filter. The Al_2O_3 combines with the alkaline fusing mixture to form a soluble potassium aluminate thus: $Al_2O_3 + K_2CO_3 = 2KAlO_2 + CO_2$. The Cr_2O_3 likewise unites with the fusing mixture in the presence of oxidizers, according to the following reaction: $Cr_2O_3 + O_3 = 2CrO_3$; then $2CrO_3 + 2K_2CO_3 = 2K_2Cr_2O_4 + 2CO_2$. The oxidizer in this case is KNO_3; $KClO_3$ acts similarly.

When the ppt. is fused, the Mn is oxidized to green potassium manganate (K_2MnO_4); this being soluble in the water interferes with detection of the Al and Cr. This green solution is therefore treated with alcohol, drop by drop, until the green color is discharged. The alcohol is reduced to aldehyd, which in turn reduces the manganese to mangano-manganic oxid (Mn_2O_3), which then precipitates and should be filtered out before testing for Al and Cr.

21. Aluminate of potassium ($KAlO_2$) is colorless; chromate of potassium (K_2CrO_4) is yellow; manganate of potassium (K_2MnO_4) is green, but after boiling in water it becomes pink.

22. The portion of the solution reserved for the detection of Cr will be yellow from the presence of K_2CrO_4, indicating Cr.

The object of acidifying the solution with acetic acid is to convert the carbonates into acetates; if this were not done, brown argentic oxid and white plumbic carbonate would be precipitated.

23. Neutralization is done with HCl, which at the same time forms aluminum chlorid, and from which NH_4OH throws

out aluminum hydroxid as a gelatinous precipitate, $Al_2(OH)_6$, insoluble in excess.

24. The metals are precipitated as sulfids, their identity being indicated by the color of the precipitate, thus: MnS, flesh-colored; ZnS, white; CoS and NiS, black. Excess of $(NH_4)_2S$ should be carefully avoided, as it dissolves some of the NiS (in which case the filtrate is brownish black). A black filtrate is evaporated and the precipitate in the form of black NiS is reclaimed. HCl dissolves all the sulfids; the NH_4OH being added to neutralize the HCl, the solution next being re-acidified with $HC_2H_3O_2$, and H_2S passed through the solution. Acetic acid is used in this case, as stronger acids would prevent the precipitation of ZnS, NiS, and CoS.

25. If the solution is not black, Co and Ni need not be sought for. If the precipitate is white = Zn.

The HCl converts the hydroxids of Co and Ni into chlorids, and the KCy forms double cyanid salts of Co and Ni; on the addition of the chlorinated soda the insoluble Ni is left, while the Co dissolves.

26 and 27. See borax-bead reactions for cobalt and nickel.

28. The fusing mixture is KNO_3 and Na_2CO_3.

SPECIAL TESTS FOR METALS OF GROUP III.

(Alkali Sulphid Group.)

To be applied to separate portions of the solution.

48. Ferric Salts.

$(NH_4)_2S$ precipitates from alkaline solutions (FeS + S), a black ppt.; the FeS is soluble in HCl:

$$Fe_2Cl_6 + 3(NH_4)_2S = \underbrace{2FeS}_{\text{Ferrous Sulfid.}} + S + 6NH_4Cl.$$

1° *K_4FeCy_6 Test.*—K_4FeCy_6 gives a deep blue ppt. of Fe_7Cy_{18} or $Fe_4(FeCy_6)_3$, insoluble in acids:

$$2Fe_2Cl_6 + 3K_4FeCy_6 = \underbrace{Fe_4(FeCy_6)_3}_{\text{Ferric Ferrocyanid.}} + 12KCl.$$

2° *K_3FeCy_6 Test.*—K_3FeCy_6 gives a brown solution:

$$Fe_2Cl_6 + 2K_3FeCy_6 = Fe_2(FeCy_6)_2 + 6KCl:$$

3° *Hydroxid Test.*—Both NaOH and NH_4OH = brown ppt., insoluble in excess:

$$Fe_2Cl_6 + 6NH_4OH = \underbrace{Fe_2(OH)_6}_{\text{Ferric Hydroxid.}} + 6NH_4OH.$$

4° *Sulfocyanid Test.*—KSCy = blood-red coloration:

$$Fe_2Cl_6 + 6KSCy = \underbrace{Fe_2(SCy)_6}_{\text{Ferric Sulfocyanid.}} + 6KCl.$$

49. Ferrous Salts.

$(NH_4)_2S$ precipitates from alkaline solutions FeS soluble in HCl and quickly oxidized in the solution to $FeSO_4$:

$$FeCl_2 + (NH_4)_2S = \underbrace{FeS}_{\substack{\text{Ferrous}\\ \text{Sulfid.}}} + 2NH_4Cl.$$

1° *Ferrocyanid Test.*—K_4FeCy_6 = white ppt. (distinction from ferric), rapidly becoming blue:

$$2FeCl_2 + 2K_4FeCy_6 = 2FeK_2FeCy_6 + 4KCl.$$

2° *Ferricyanid Test.*—K_3FeCy_6 = deep-blue ppt. insoluble in acids:

$$3FeCl_2 + 2K_3FeCy_6 + \underbrace{Fe_3Fe_2Cy_{12}}_{\text{Ferrous Ferricyanid.}} + 6KCl.$$

3° *Sulfocyanid Test.*—No red coloration (distinction from ferric).

50. Cobalt

In alkaline solutions gives a black ppt. of CoS with $(NH_4)_2S$:

$$Co(NO_3)_2 + (NH_4)_2S = \underbrace{CoS}_{\text{Cobalt Sulfid.}} + 2NH_4NO_3.$$

1° *Ammonia Test.*—NH_4OH = a blue ppt. of $Co(OH)_2$ soluble in excess to a brown solution, and reprecipitated by NaOH:

$$Co(NO_3)_2 + 2NH_4OH = \underbrace{Co(OH)_2}_{\text{Cobalt Hydroxid.}} + 2NH_4NO_3.$$

2° *Borax-bead Test* gives a blue bead.

3° *Cyanid Test.*—KCy = a brown ppt. of $CoCy_2$ soluble in excess on boiling and not precipitated by chlorinated soda solution (distinction from nickel).

4° *Sodium Hydroxid Test.*—NaOH = a blue ppt. of $Co(OH)_2$, changed to red on boiling.

51. Nickel.

Precipitated from alkaline solutions by $(NH_4)_2S$ = a black ppt. of NiS, nearly insoluble in dil. HCl:

$$NiSO_4 + (NH_4)_2S = \underbrace{NiS}_{\text{Nickel Sulfid.}} + (NH_4)_2SO_4.$$

1° *Sodium-hydroxid Test.*—$NaOH$ = a green ppt. insoluble in excess, not changed by boiling:

$$NiSO_4 + 2NaOH = \underbrace{Ni(OH)_2}_{\text{Nickel Hydroxid.}} + Na_2SO_4.$$

2° *Ammonia Test.*—NH_4OH gives a precipitate similar to 1°, but soluble in excess of the reagent, forming a violet-colored solution.

3° *Cyanide Test.*—KCy = a pale green ppt. soluble in excess. When boiled with chlorinated soda solution = a black ppt.:

$$NiSO_4 + 2NH_4OH = Ni(OH)_2 + (NH_4)_2SO_4.$$

4° *Borax-bead Test.*—Purplish brown hot; pinkish brown cold.

52. **Zinc.**

Precipitated in presence of NH_4Cl from alkaline solutions by $(NH_4)_2S$ as ZnS = a white ppt. soluble in HCl:

$$ZnSO_4 + (NH_4)_2S = \underbrace{ZnS}_{\text{Zinc Sulfid.}} + (NH_4)_2SO_4.$$

1° *Cobalt Test.*—Heat a portion of the solution on charcoal with a drop or two of $Co(NO_3)_2$ solution = a green mass which is infusible.

2° *Ferrocyanid Test.*—K_4FeCy_6 gives a white gelatinous ppt. of Zn_2FeCy_6 insoluble in diluted acids:

$$2ZnSO_4 + K_4FeCy_6 = Zn_2FeCy_6 + 2K_2SO_4.$$

53. **Aluminum.**

$(NH_4)_2S$ precipitates from alkaline solutions $Al_2(OH)_6$ insoluble in excess:

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = \underbrace{Al_2(OH)_6}_{\text{Aluminum Hydroxid.}} + 3(NH_4)_2SO_4 + 3H_2S.$$

1° *Phosphate Test.* — $Na_2HPO_4 + NH_4OH + HC_2H_3O_2$ = a white ppt. of $AlPO_4$ insoluble in hot $HC_2H_3O_2$, but soluble in HCl:

$$Al_2(SO_4)_3 + 2H_3PO_4 = \underbrace{2AlPO_4}_{\substack{\text{Aluminum}\\ \text{Phosphate.}}} + 3H_2SO_4.$$

2° *Hydroxid Test.*—Both NH_4OH and NaOH give a gelatinous white ppt. soluble in excess, with the former only slightly soluble:

$$Al_2(SO_4)_3 + 6NaOH = \underbrace{Al_2(OH)_6}_{\substack{\text{Aluminum}\\ \text{Hydroxid.}}} + 3Na_2SO_4.$$

3° *Cobalt Test.*—$Co(NO_3)_2$ added to a portion heated on charcoal gives an infusible blue mass.

54. **Manganese.**

Precipitated from alkaline solutions by $(NH_4)_2S$ as MnS, a flesh-colored ppt. soluble in diluted HCl or $HC_2H_3O_2$:

$$MnSO_4 + 2(NH_4)_2S = \underbrace{MnS}_{\substack{\text{Manganese}\\ \text{Sulfid.}}} + 2(NH_4)_2SO_4.$$

1° *Lead Test.*—PbO_2 heated with some of the substance and HNO_3 (until free from nitrous fumes) and poured into H_2O gives a purple solution of permanganate:

$$2MnSO_4 + 4HNO_3 + 3PbO_2$$
$$= \underbrace{H_2Mn_2O_8}_{\text{Permanganic Acid.}} + 2PbSO_4 + Pb(NO_3)_2 + N_2O_3 + H_2O.$$

2° *Alkaline-hydroxid Test.*—NaOH or KOH = a white ppt. of $Mn(OH)_2$, which becomes brown upon heating:

$$MnSO_4 + 2NaOH = \underbrace{Mn(OH)_2}_{\text{Manganese Hydroxid.}} + Na_2SO_4.$$

3° *Carbonate Test.*—Heated on a platinum wire with some Na_2CO_3 gives a green mass.

4° *Borax-bead Test.*—Bead in O flame is purple-colored.

55. Chromium.

$(NH_4)_2S$ precipitates from alkaline solutions $Cr_2(OH)_6$ = a green ppt. soluble in diluted HCl:

$$Cr_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = \underbrace{Cr_2(OH)_6}_{\text{Chromium Hydroxid.}} + 3(NH_4)_2SO_4 + 3H_2S.$$

1° *Sodium-hypochlorite Test.*— Chlorinated soda solution ($NaClO + NaCl$) boiled with an alkaline chromium salt gives a yellow solution of sodium chromate, (Na_2CrO_4).

2° *Sodium-hydroxid Test.*—NaOH = a bluish-green ppt. of $Cr_2(OH)_6$ soluble in excess, and reprecipitated on boiling:

$$Cr_2(SO_4)_3 + 6NaOH = \underbrace{Cr_2(OH)_6}_{\text{Chromium Hydroxid.}} + 3Na_2SO_4.$$

3° *Borax-bead Test.*—The bead is emerald-green in color.

56. CHART FOR THE SEPARATION OF GROUP IV.

29. To the alkaline filtrate from Group III add some solution of $(NH_4)_2CO_3$, warm and allow to rest a few minutes; if a precipitate occurs, it may contain

Ba, Sr, Ca.

30. Collect, wash, and dissolve it on the filter with a small quantity of acetic acid. To the filtrate add some solution of K_2CrO_4; if a precipitate occurs, filter.

- **31. Precipitate.** Ba = yellow ppt. Confirm by dissolving ppt. in HCl and flame test. Green-colored flame = Ba.
- **32. Solution.** Sr, Ca. Add to this some dil. H_2SO_4 (1 : 50), shake well and filter.
  - **33. Precipitate.** Sr. Confirm by moistening the ppt. with HCl and applying flame test. Crimson-colored flame = Sr.
  - **34. Solution.** Ca. Neutralize with NH_4OH, add $(NH_4)_2C_2O_4$: a white ppt. = Ca.

57. OBSERVATIONS ON GROUP IV.

29. The metals of this group are precipitated as carbonates, thus: $BaCO_3$, $SrCO_3$, $CaCO_3$. Magnesium carbonate is not precipitated here on account of its being present as a double magnesium-ammonium soluble compound ($MgCl_2.2NH_4Cl$.)

The solution with the precipitated carbonates should only be warmed, *not boiled.* If the mixture be boiled, the precipitated carbonates are decomposed into chlorids through the presence of the magnesium-ammonium compound, and may later be mistaken for magnesium when Na_2HPO_4 is added for the detection of that metal.

The above-mentioned decomposition into chlorids is explained by the following two reactions:

$$(1)\quad CaCl_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4Cl.$$

$$(2)\quad CaCO_3 + 2NH_4Cl = CaCl_2 + (NH_4)_2CO_3.$$

58. NOTES ON GROUP IV.

30. When the precipitated carbonates are treated with acetic acid, acetates of the metals are formed with the evolution of CO_2.

When neutral potassium chromate is added, barium is separated as yellow barium chromate ($BaCrO_4$).

31. See paragraph 59.

32. The exact separation of the calcium and strontium is tedious. The following simple method based on the solubilities in water of $SrSO_4$ (1 in 7000) and $CaSO_4$ (1 in 400) is usually employed: To a small portion of the filtrate add some saturated solution of $CaSO_4$ and set the mixture aside for some time. If strontium be present, $SrSO_4$ (a white ppt.) will be obtained. To another portion add some very dilute H_2SO_4 (1 in 50) and set aside for complete deposition of $SrSO_4$ (this will contain some $CaSO_4$).

33. Apply the flame test for the strontium (crimson flame).

34. If the least trace of calcium be present in the filtrate, a white precipitate of calcium oxalate insoluble in water and acetic acid is obtained on the addition of ammonium oxalate.

SPECIAL TESTS FOR METALS OF GROUP IV.

(CARBONATE GROUP.)

To be applied to separate portions of the solution.

59. **Barium.**

Precipitated from alkaline solutions (previously heated) by $(NH_4)_2CO_3$, $= BaCO_3$; soluble in acids:

$$BaCl_2 + (NH_4)_2CO_3 + 2NH_4Cl = \underbrace{BaCO_3}_{\text{Barium Carbonate}}.$$

1° *Sulfate Test.*—K_2SO_4 or $CaSO_4$ = a white ppt. of $BaSO_4$ insoluble in acids:

$$BaCl_2 + K_2SO_4 = \underbrace{BaSO_4}_{\text{Barium Sulfate.}} + 2KCl.$$

2° *Chromate Test.*—K_2CrO_4 = a yellow ppt. of $BaCrO_4$ insoluble in $HC_2H_3O_2$:

$$BaCl_2 + K_2CrO_4 = \underbrace{BaCrO_4}_{\text{Barium Chromate.}} + 2KCl.$$

3° *Oxalate Test.* — $(NH_4)_2C_2O_4$ = a white ppt. soluble in $HC_2H_3O_2$:

$$BaCl_2 + (NH_4)_2C_2O_4 = \underbrace{BaC_2O_4}_{\text{Barium Oxalate.}} + 2NH_4Cl.$$

4° *Flame Test.*—Barium salts heated with HCl on a platinum wire = a green flame.

60. Strontium.

Precipitated from hot alkaline solutions by $(NH_4)_2CO_3$ = a white ppt. soluble in acids:

$$Sr(NO_3)_2 + (NH_4)_2CO_3 = \underbrace{SrCO_3}_{\text{Strontium Carbonate.}} + 2NH_4NO_3.$$

1° *Chromate Test.*—$K_2Cr_2O_7$ = no precipitate except in very concentrated solutions.

2° *Sulphate Test.*—K_2SO_4 or $CaSO_4$ = a white ppt. of $SrSO_4$ (which forms very slowly, and is more soluble than $BaSO_4$):

$$Sr(NO_3)_2 + CaSO_4 = SrSO_4 + Ca(NO_3)_2.$$

3° *Flame Test.*—Strontium salts heated with HCl on a platinum wire = a crimson-red flame.

61. Calcium.

Precipitated from hot alkaline solutions by $(NH_4)_2CO_3$ = a white ppt. of $CaCO_3$ soluble in acids:

$$CaCl_2 + (NH_4)_2CO_3 = \underbrace{CaCO_3}_{\text{Calcium Carbonate.}} + 2NH_4Cl.$$

1° *Oxalate Test.*—$(NH_4)_2C_2O_4$ = a white ppt. of CaC_2O_4 nearly insoluble in $HC_2H_3O_2$:

$$CaCl_2 + (NH_4)_2C_2O_4 = \underbrace{CaC_2O_4}_{\text{Calcium Oxalate.}} + 2NH_4Cl.$$

2° *Sulfate Test.*—K_2SO_4 in concentrated solutions = a white ppt. of $CaSO_4$.:

$$CaCl_2 + K_2SO_4 = \underbrace{CaSO_4}_{\text{Calcium Sulfate.}} + 2KCl.$$

62. GROUP V.

35. Divide the filtrate from Group IV into two portions, one larger than the other. To the smaller portion add some NH_4OH and Na_2HPO_4. A white precipitate indicates *magnesium*.

36. Evaporate the larger portion to dryness and ignite; if *no residue*, K, Na, and Li are absent. If *residue*, dissolve it in a few drops of water, place on a watch-glass, acidulate with HCl and add solution $PtCl_4$. A yellow ppt. = potassium.

37. Heat a little of the original substance or solution with sol. of KOH, NaOH, or $Ca(OH)_2$. Odor of ammonia indicates ammonium.

38. Apply a little of the solution from 36, or some of the original substance on a platinum wire, to the colorless gas flame and observe

63. *The Color of the Flame.*

Yellow....................	Sodium compounds.
Red........................	Calcium or lithium compounds.
Crimson....................	Strontium compounds.
Violet (through blue glass)..	Potassium compounds.
Blue.......................	Lead, arsenic, antimony.
Green......................	Barium, copper, or boric acid.
Greenish white.............	Zinc.

64. OBSERVATIONS AND NOTES ON GROUP V.

The filtrate from Group IV contains only the salts of Mg, K, Na, Li, and NH_4.

35. The object of adding NH_4OH before the Na_2HPO_4 is to render the ppt. less soluble in water.

If magnesium be present, it is indicated by a crystalline precipitate of ammonio-magnesium phosphate ($MgNH_4PO_4$).

This precipitate appears only on standing. Any non-crystalline precipitate is calcium which may have escaped from the previous group.

36. The residue in this case is ignited to dissipate the NH_4 compounds, since these form insoluble double chlorids with platinic chlorid ($PtCl_4$).

The ignited residue may contain Mg, if its presence has been detected in the smaller quantity of the liquid. The yellow precipitate formed with K is a double chlorid of potassium and platinum ($2KCl.PtCl_4$).

With sodium a corresponding soluble salt is formed which gives an intense yellow coloration to the flame.

SPECIAL TESTS FOR METALS OF GROUP V.

To be applied to separate portions of the solution.

65. Magnesium.

Precipitated from its alkaline ammonium-chlorid solution by Na_2HPO_4 as $MgNH_4PO_4$ = a white ppt., from concentrated solutions, and a crystalline ppt. from dilute solutions:

$$MgSO_4 + NH_4OH + Na_2HPO_4 = \underbrace{MgNH_4PO_4}_{\substack{\text{Ammonio-magnesium} \\ \text{Phosphate.}}} + Na_2SO_4 + H_2O.$$

1° *Alkaline-hydroxid Test.*—Both $NaOH$ and NH_4OH = a white ppt. of $Mg(OH)_2$ soluble in NH_4Cl:

$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4.$$

2° *Charcoal Test.*—Heated on charcoal with a drop or two of $Co(NO_3)_2$ solution, leaves a pinkish mass.

3° *Carbonate Test.*—Sodium carbonate produces a white ppt. of basic magnesium carbonate, soluble in NH_4Cl.

66. Potassium.

1° *Alkaline-tartrate Test.*—$NaHC_4H_4O_6$ = a white crystalline ppt. of $KHC_4H_4O_6$ (in concentrated solutions only). This is a distinguishing test between potassium and sodium, the latter not giving a ppt. with alkaline tartrate:

$$KNO_3 + NaHC_4H_4O_6 = \underbrace{KH_4H_4O_6}_{\substack{\text{Potassium-hydrogen} \\ \text{Tartrate.}}} + NaNO_3.$$

2° *Platinum-chlorid Test.*—$PtCl_4$ = a yellow ppt. of K_2PtCl_6 soluble in excess of water (distinction from Na):

$$2KCl + PtCl \; = \underbrace{K_2PtCl_6}_{\substack{\text{Double Potassio-}\\\text{platinic Chlorid.}}}.$$

3° *Sodium-Cobaltic-nitrite Test.*—$NaNO_2.Co(NO_2)_2$ in presence of $HC_2H_3O_2$ = a yellow crystalline ppt.

4° *Flame Test.*—Potassium salts heated with HCl on a platinum wire = a violet coloration when viewed through a blue glass.

67. Sodium.

1° *Alkaline-tartrate Test*—$NaHC_4H_4O_6$ = no precipitate (distinction from potassium).

2° *Platinum-chlorid Test.*—$PtCl_4$ = no precipitate with sodium salt (distinction from potassium).

3° *Antimony Test.*—$K_2Sb_2O_6$ = a white crystalline ppt. of $Na_2Sb_2O_6$ (metantimonate) in neutral solutions only and on vigorous shaking:

$$2NaCl + K_2Sb_2O_6 = \underbrace{Na_2Sb_2O_6} + 2KCl.$$

4° *Flame Test.*—Sodium salts with HCl heated on platinum wire give intense yellow coloration to the flame (invisible through blue glass).

68. Lithium.

1° *Phosphate Test.*—Na_2HPO_4 in boiling solutions = a white ppt. of Li_3PO_4:

$$3LiCl + Na_2HPO_4 = \underbrace{Li_3PO_4}_{\substack{\text{Lithium}\\\text{Phosphate.}}} + 2NaCl + HCl.$$

2° *Carbonate Test.*—Na_2CO_3 in concentrated solutions = Li_2CO_3:

$$2LiCl + Na_2CO_3 = \underbrace{Li_2CO_3}_{\text{Lithium Carbonate.}} + 2NaCl.$$

3° *Flame Test.*—Lithium salts heated with HCl on a platinum wire = a bright-red flame.

69. **Ammonium.**

1° *Alkaline-tartrate Test.*—$NaHC_4H_4O_6$ = white ppt.:

$$NH_4Cl + NaHC_4H_4O_6 = \underbrace{NH_4HC_4H_4O_6}_{\text{Ammonium Acid Tartrate.}} + NaCl.$$

2° *Platinic-chlorid Test.*—$PtCl_4$ = a yellow ppt. of $(NH_4)_2PtCl_6$ (in concentrated solutions):

$$2NH_4Cl + PtCl_4 = \underbrace{(NH_4)_2PtCl_6}_{\text{Double Ammonio-platinic Chlorid.}}.$$

3° *Hydroxid Test.*—Either NaOH or $Ca(OH)_2$ heated with some of the solution gives off NH_3 (detected by the smell). This vapor turns red litmus paper blue:

$$NH_4Cl + KOH = \underbrace{NH_3}_{\text{Gas.}} + KCl + H_2O.$$

Hold a glass rod moistened with HCl over the mouth of the test-tube: white fumes of NH_4Cl are formed:

$$NH_3 + HCl = \underbrace{NH_4Cl}_{\text{Ammonium Chlorid.}}.$$

4° *Nessler's Test.*—Nessler's reagent (made from $HgCl_2$ + KI till ppt. dissolves, then NaOH in excess) gives a yellow or brownish ppt. of NHg_2I (di-mercuric ammonium iodid).

$$NH_3 + 2HgI_2 + 3NaOH = NHg_2I + 3NaI + 3H_2O$$

70. CHART FOR THE SEPARATION OF INSOLUBLE PHOSPHATES.

39. If the precipitate in Group III contains phosphates (proved by ammonium molybdate test), dissolve the precipitate in a very small quantity of HCl, add some $NaC_2H_3O_2$ and then some solution Fe_2Cl_6. Boil for five minutes and filter. (The ppt. contains the insoluble phosphates of iron, chromium, and aluminum.)

The filtrate is tested for the ordinary metals of the third and fourth groups in the usual manner.

Fuse the ppt. well with KNO_3 and Na_2CO_3, treat with boiling water and filter. Test a portion of the filtrate for Cr with a solution of $AgNO_3$; a red ppt. = Cr. The remainder of the filtrate is next acidified with HCl, and an excess of NH_4OH added; a white flocculent ppt. = Al. The residue on the filter is dissolved with a few drops of hot aqua regia, diluted with water, and added to some KCyS solution; a blood-red coloration = Fe.

40. If the original substance is insoluble and was found to contain phosphates, employ the following chart:

Boil some of the substance with a very small quantity of HCl, add cold NaOH in excess, filter. The residue will contain the iron and other insoluble phosphates. Digest with cold acetic acid and filter.

Insoluble.
$FePO_4$.
Reddish-white ppt.

Soluble.
Phosphates of Al, Cr, Co, Ni, Zn, Mn, Ba, Sr, Ca, Mg.
Add Fe_2Cl_6, drop by drop, until a pale-reddish tint is obtained. Heat for some time and filter while hot.

Insoluble.
$FePO_4$.

Soluble.
Members of Group III and IV to be proved in the ordinary way.

NOTE.—The important insoluble (in water and acids) substances which may be found in the insoluble residues are: C, S, $BaSO_4$, $SrSO_4$, $CaSO_4$, $PbSO_4$, $PbCl_2$, AgCl, CaF_2, silica and silicates, and native oxids of Al, Cr, Fe, and Sn. Special tests should be applied to identify these.

71. *Color of Borax Beads.*—Borax, $Na_2B_4O_7$, when ignited on a loop of a platinum wire forms a bead, known as *borax bead*, which when dipped in certain compounds or their solutions yields a colored glass useful for the detection of many of the metallic compounds, thus:

In the Oxidizing Flame.		In the Reducing Flame.		Indicates
Hot.	Cold.	Hot.	Cold.	
Green	Blue	....	Red	Cu
Blue	......	Blue	......	Co
Green	......	Green	......	Cr
Red	Yellowish	Bottle-green	......	Fe
Amethyst	......	Colorless	......	Mn
Purple-brown	Pink-brown	Reddish brown	Yellow	Ni

72. PREPARATION OF A SOLUTION FOR ANALYSIS IN THE WET WAY.

To confirm the results obtained by the dry examination of all solid substances, except simple ones that yield positive results in the dry way, the matter of getting these into solution becomes of importance.

To bring into play the natural force called chemical affinity, substances must be brought into close contact with one another, and this condition can best be brought about in a solution. For analytical purposes all substances may be divided into four classes, as follows:

1. Substances soluble in water.
2. Substances insoluble in water but soluble in an acid.
3. Substances insoluble in an acid but soluble in a mixture of acids.
4. Substances decomposed by fusing with carbonates.

Complex substances may contain compounds belonging to each of the above four classes. A small portion is heated with some water in a test-tube and filtered; the filtrate is now

tested for compounds which may have gone into solution. The residue is next treated with an acid, the excess of the acid evaporated off, the substance diluted with water and filtered, and the filtrate tested for substances that may have been dissolved, etc. The order most frequently followed is: 1st, water; 2d, hydrochloric acid, dilute; 3d, HCl concentrated; 4th, nitric acid, dilute; 5th, HNO_3 concentrated; 6th, nitro-hydrochloric acid; 7th, sulfuric acid.

In using acids as solvents care must be taken not to use them in excess; if, however, an excess has been used, evaporate the solution under a hood to drive off the excess of acid. If the acid is the proper solvent, very little of it will dissolve a large quantity of the substance.

If, after going through the above-mentioned list of acid solvents, the substance still remains insoluble, it may consist of $BaSO_4$, $PbSO_4$, C, S, oxids of tin, silica and silicates, fluorids, alumina and aluminates, Sb_2O_3 and Sb_2O_5, chrome iron ore, some metaphosphates, arsenates, silver chlorid, etc. Fuse a small portion of the powder with about five times its bulk of a fusion mixture ($Na_2CO_3 + KNO_3$) in a small crucible (preferably platinum), extract the fused mass with water, and filter. Dissolve what remains on the filter in HCl; if this does not effect solution, try HNO_3.

NOTE 1. If the preliminary examination shows absence of Pb, boil the powder with NaOH solution, thus avoiding the more difficult and tedious fusion.

The action of the fusion mixture in the above operation is, generally speaking, to convert the base into an oxid or a carbonate, the acid of the substance combining with the Na and K as a corresponding salt.

NOTE 2. It should be remembered that the excess of any acid solvents must be removed before proceeding to examine for metals of the second group; strong acids (*a*) decompose H_2S into its elements and (*b*) prevent the precipitation of some of the metals.

Above all it should be borne in mind that:

(1) If the substance is solid, it must be finely powdered before effecting solution.

(2) That each solvent should be tried first cold, and then, if required, hot.

(3) The solution for analysis should be neutral or just slightly acid. If alkaline, neutralize with HNO_3, any precipitate produced being filtered off and examined separately.

(4) Since cyanids, ferrocyanids, cobalticyanids, etc., greatly interfere with the ordinary processes of analysis, it is best to destroy them before proceeding, by evaporating some of the solution to dryness with H_2SO_4, whereby all the metals will be obtained as sulfates.

(5) If the substance is a hard metal or alloy, treat it as under "Alloys and Hard Metals".

73. ALLOYS AND HARD METALS.

Procedure.—Cut the alloy into very small pieces, or file off 2 grams of it, or hammer it out flat so as to expose the largest possible surface to the action of the acid. Heat about 2 grams of the thus-prepared substance with about 40 c.c. of strong HNO_3 in a capsule, evaporate to small bulk to remove excess of acid, dilute with H_2O, and filter.

- **Insoluble.** SnO_2 and Sb_2O_5 (as hydroxids or as arsenates). [Also possibly Bi as arsenate or phosphate, and Au and Pt.] Digest with zinc and dilute HCl. Test the evolved gases for arsine by the $AgNO_3$ test. Residue on the zinc may consist of the remaining metals. Boil for some time with strong HCl under hood, and filter.
  - **Insoluble.** Sb [Bi, Au, Pt.] Digest with yellow $(NH_4)_2S$; Sb dissolves as sulfo-salt. Evaporate solution to dryness. Orange-red residue = *antimony.*
  - **Soluble.** $SnCl_2$. Add $HgCl_2$. White ppt., turning gray on heating = tin.
- **Soluble.** Apply the usual group reagents and identify the metals in the groups.

74. SOLUBILITIES.—Table Showing the Solubility of the More Commonly Occurring Salts.

Name.	Soluble in Water.	Soluble in, or Decomposed by, Acids.	Insoluble.
Carbonates.	Acid carbonates of Ba, Sr, Pb, Mn, Mg, Fe″, and Ca, and alkaline carbonates.	All carbonates are decomposed with evolution of CO_2.	
Sulfates.	Most sulfates. (Ag_2SO_4 is difficultly soluble.)	Some *basic* sulfates.	Sulfates of Pb, Ba, Sr, and Ca, and red chromic sulfate.
Nitrates.	Most nitrates (a few *basic* nitrates excepted).	A few basic nitrates which are readily soluble in dilute HNO_3.	
Chlorids.	Most chlorids.	A few oxychlorids. (BiOCl and SbOCl.)	Chlorids of Pb, Hg′, Ag, and Cu_2Cl_2.
Bromids.	Most bromids.	Cu_2Br_2 in HCl.	Bromids of Hg′, Ag, and Pb.
Iodids.	Most iodids.	HgI_2, Hg_2I_2 ($=HgI_2+Hg$), PbI_2, Cu_2I_2 decomposed by HNO_3 with evolution of I.	Iodids of Ag, Hg′, Hg″, Pb, and Cu′.
Chlorates.	All chlorates.		
Sulfids.	Alkaline and alkaline-earthy sulfids. MgS and CaS *very slightly* soluble.	All other sulfids are decomposed by HCl (H_2S being evolved), or by HNO_3, or aqua regia, with separation of S.	
Phosphates.	Alkaline phosphates only.	Remainder are soluble.	
Chromates.	Alkaline chromates and chromates of Mg, Zn, Ca, Sr, Fe^{iv}, and Cu.	Chromates insoluble in water dissolve in acids (evolving chlorin in concentrated HCl).	Ignited lead chromate.

75. THE IDENTIFICATION OF ACIDS AND ACIDULOUS RADICALS.

Acids are divided into two classes: (*a*) Inorganic, (*b*) Organic. The tests applied below are intended to be applied to salts of the alkaline metals, for only in such combination can reliable results be obtained in testing for the acids. Therefore if the acid or its radical is not in combination with an alkaline metal, it is a general rule to convert it into a salt of sodium, by boiling with $NaOH$. The ppt., if any, should be separated by filtration and the filtrate tested.

(*a*) If the salt is soluble in water and neutral or alkaline in reaction, the boiling with $NaOH$ is generally not needed.

(*b*) If the substance is insoluble in water but soluble in acids, boil a portion of the solid with a strong solution of sodium carbonate, filter, and use the filtrate.

(*c*) If the substance is insoluble, treat as described for the preparation of the solution for analysis of insoluble substances, using the filtrate, which is neutralized with NH_4OH.

(*d*) In those cases where the metal present is one whose hydroxid is soluble, and which cannot in consequence be removed by treatment with $NaOH$, it is necessary to use, instead of the latter, Na_2CO_3, boil, and neutralize with HNO_3.

76. **Preliminary Examination for Acids.** — The following tests are to be made upon small portions of the dry substance. If the substance is in the form of a solution, a small portion of it is carefully evaporated to dryness and the following test applied:

Heat a small portion of the dry substance in a small test-tube with four times its bulk of strong H_2SO_4 and observe effect.

1° No action ensues. Indication: Silicic, phosphoric, iodic, molybdic, sulfuric, boric (arsenic and chromic found as bases) acids.

2° Vapors are evolved:

	Indication.
Violet, coloring starch mucilage *blue*. .	Iodic acid.
Reddish, " " " *orange*	Bromic acid.
Greenish yellow, *explosive*.	Chloric acid.
Yellow, smell of (Cl_2O), "*euchlorin*". .	Hypochlorous acid.
Brownish yellow, *irritating*.	Nitrous or nitric.

3° Gases ensue (colorless):

	Indication.
With odor of *acetic acid*.	Acetic acid.
" " " *rotten eggs*.	Hydrosulfuric acid.
" " " *burning sulfur*.	Sulfurous acid. Thiosulfuric acid.
" " " *peach kernels*.	Hydrocyanic acid. Ferrocyanic acid.
" " " *burnt sugar*.	Tartaric acid.
" irritating odor; white fumes with NH_4OH	Hydrochloric acid.
Fuming, *etching glass*.	Hydrofluoric acid.
Oxygen; color changes to *brown*.	Chromic acid.
Odorless; turbid, when shaken with *lime-water*.	Carbonic acid.
Odorless; burns with *blue flame,* and renders *lime-water turbid*	$= CO + CO_2 =$ Oxalic acid.

77. SYSTEMATIC DETECTION OF THE ACIDS IN SOLUTIONS.

As stated in paragraph 75, acids are divided into two great classes, the *inorganic* and the *organic*. These are readily distinguished by the action of heat.

Salts of *inorganic acids* when heated to redness are not charred; salts of *organic acids* (with the exception of acetic, formic, and oxalic) are at once charred, owing to decompo-

sition and separation of *carbon,* which fact also applies to all organic substances.

The acids do not admit of being grouped as precisely as do the bases; they can, however, be approximately classified by means of appropriate group reagents, thus:

GROUP I. REAGENT $BaCl_2$ in presence of HCl.
The acids of this group are precipitated by $BaCl_2$, and the precipitate is not dissolved on the addition of HCl.
Members of the Group: Sulfuric acid and hydrofluosilicic acid.

GROUP II. REAGENT $BaCl_2$.—The acids of the second group are precipitated by $BaCl_2$ *in neutral solutions only.* The precipitate is soluble in HCl.
Members of Group II: Phosphoric, boric, oxalic, hydrofluoric, carbonic, silicic, sulfurous, thiosulfuric, arsenous, arsenic, iodic, and chromic acids.

GROUP III. REAGENT $AgNO_3$.—Members of this group are precipitated by $AgNO_3$, but not by $BaCl_2$.
Members of Group III: Hydrochloric, hydrobromic, hydriodic, hypochlorous, hydrocyanic, and hydrosulfuric acids.

GROUP IV. NON-PRECIPITABLE ACIDS.—Acetic, chloric, nitric, and perchloric. Acids of this group form with bases soluble compounds and are not precipitated by any reagent.

78. Having located to which group the acid belongs, systematic confirmatory tests for members of such group are applied, found in the following tables under Indication.

(A) To a portion of the original add H_2SO_4 (warm if necessary).

Result.	Indication.	Confirmatory Tests to be Applied to Some of the Original Solution.
Effervescence without odor.	Carbonate or	Fe_2Cl_6, red ppt.—$MgSO_4$, white ppt. at once.
	Bicarbonate.	Fe_2Cl_6, red ppt.—$MgSO_4$, no ppt., but ppt. on boiling.
Odor of vinegar.	Acetate.	Fe_2Cl_6, red coloration destroyed by HCl. Alcohol + H_2SO_4 + heat = odor acetic ether.
Odor of rotten eggs.	Sulfid.	$Fe_2Cl_6 + NH_4OH$ = black ppt.
Odor of burning sulfur.	Sulfite.	HCl and warm, SO_2 evolved; no ppt Add $AgNO_3$, white ppt.; warm it = black ppt.
	Thiosulfate.	HCl and warm, SO_2 evolved *and white ppt.* of S. Add $AgNO_3$, white ppt.; warm it = black ppt.
Odor of hydrocyanic acid.	Cyanid.	$FeSO_4$, red ppt. One drop $FeSO_4$ to excess of solution, then Fe_2Cl_6 and HCl = Prussian blue.
	Ferrocyanid.	$FeSO_4$, light-blue ppt.—Fe_2Cl_6 = Prussian blue.
	Ferridcyanid.	$FeSO_4$, dark-blue ppt.; Fe_2Cl_6 = no ppt., but coloration.
Odor of benzoic acid.	Benzoate.	Fe_2Cl_6, pale-buff color and ppt.
Odor of phenol.	Carbolate.	Fe_2Cl_6, violet color; evaporate to dryness, ignite residue, dissolve in HCl, no ppt. with $BaCl_2$.
	Phenolsulfonate.	Fe_2Cl_6, violet color; evaporate to dryness, ignite residue, dissolve in HCl, white ppt. with $BaCl_2$.

(B) To a separate portion of the solution add $BaCl_2$.

Result.	Indication.	Confirmatory Tests to be Applied to Some of the Original Solution.
White ppt. insol. in HCl.	Sulfate.	If ppt. is soluble in HCl pass on to next table.

Phosphates, oxalates, carbonates, borates, sulfites, thiosulfates, chromates, silicates, and some other salts are likewise precipitated by $BaCl_2$, but the ppt. so produced is in each case soluble in, or decomposed by, HCl; hence the foregoing test is distinctive of sulfates.

(C) To a separate portion of the solution (rendered neutral) add $CaCl_2$.

Result.	Indication.	Confirmatory Tests to be Applied to Some of the Original Solution.
White ppt. at once insol. in $HC_2H_3O_2$.	Oxalate.	If ppt. *is* sol. in $HC_2H_3O_2$ pass on to next table.
* White ppt. on shaking	Tartrate.	$AgNO_3$ to neutral solution, 1 drop of NH_4OH; boil, mirror is produced.
* White ppt. on boiling.	Citrate.	$AgNO_3$ to neutral solution and 1 drop NH_4OH, boil; no mirror is produced.

* If the precipitate of this group does not answer above, pass on to Table E; likewise remember that the last three tests are applied only where preliminary tests show presence of organic matter.

(D) To a separate portion of the solution acidified with HNO_3 add $AgNO_3$.

Result.	Indication.	Confirmatory Tests to be Applied to Some of the Original Solution.
Yellow ppt.	Iodid.	Cl water + starch paste = blue color.
Yellowish-white ppt.	Bromid.	" " + " " = yellow "
White ppt.	Chlorid.	Ppt. soluble in NH_4OH, insol. in HNO_3.
	Cyanid and	Add 1 drop $FeSO_4 + HCl + Fe_2Cl_6$ = Prussian blue.
	Sulfocyanate.	Fe_2Cl_6. red coloration, not destroyed, + HCl.
	Ferrocyanid.	See Table (A).
Orange ppt.	Ferricyanid.	Fe_2Cl_6, no ppt., but coloration.

(E) To a separate portion of the (neutralized) solution add $AgNO_3$.

Result.	Indication.	Confirmatory Tests to be Applied to Some of the Original Solution.
Yellow ppt.	Arsenite, and	Ppt. sol. in HNO_3.—HCl and H_2S = yellow ppt.
	Phosphate.	Ppt. sol. in HNO_3.—HCl and H_2S = *no* ppt.
Dark-brown ppt.	Arsenate.	HCl strong + H_2S gas = yellow ppt. after some little time.—Apply Marsh's test.
Dark-red ppt.	Chromate, and	NH_4OH, color not altered.—HCl, color changed to red.—HCl + H_2S, green color is formed.
	Dichromate.	NH_4OH, color changed to yellow.—HCl, color not altered.—HCl + H_2S, green color is formed.
Black ppt.	Sulfid.	$AgNO_3$, black ppt., insoluble in dil. acids.—$Pb(C_2H_3O_2)_2$ produces black ppt.
White ppt., turning black on warming.	Sulfite.	See Group (A).
	Thiosulfate.	" " (A).
	Hypophosphite.	$CaCl_2$, *no* ppt.—$K_2Mn_2O_8$, color discharged without acid
	Phosphite.	$CaCl_2$, white ppt.—$K_2Mn_2O_8$, color discharged with HCl.
White ppt., forming mirror when boiled with 1 drop of NH_4OH.	Tartrate.	$CaCl_2$, white ppt. on shaking.
White ppt., forming mirror when boiled with 1 drop of $HC_2H_3O_2$.	Formate.	Fe_2Cl_6, red color, destroyed with HCl.—H_2SO_4 and warm, no odor of acetic acid.
White ppt.	Borate.	Fe_2Cl_6, faint-yellow ppt.—Evaporate to dryness, add H_2SO_4 and alcohol, ignite = green flame.
	Metaphosphate.	$HC_2H_3O_2$ and albumin, coagulation.
	Pyrophosphate.	$HC_2H_3O_2$ and albumin, no coagulation.

(F) To a separate portion of the neutralized solution add Fe_2Cl_6.

Result	Indication.	Confirmatory Tests to be Applied to Some of the Original Solution.
Red color, but no precipitate.	Acetate.	See in Table (A).
	Formate.	" " " (E).
	Sulfocyanate.	" " " (D).
	Sulfite.	" " " (A).
	Thiosulfate.	" " " (A).
	Pyrogallate.	Milk-of-lime, purple color turning brown.—Solution of gelatin, *no* ppt.
Violet color, but no precipitate.	Carbolate.	See Table (A).
	Phenolsulfonate.	" " (A).
	Salicylate.	H_2SO_4 and heat, no odor of phenol.
Greenish or brown color.	Ferricyanid.	See Table (A).
Dark-blue precipitate	Ferrocyanid.	" " (A).
Yellow precipitate.	Borate.	" " (E).
	Oxalate.	" " (C).
Black precipitate.	Sulfid.	" " (A).
	Gallate.	Milk-of-lime, brown color quickly formed.—Sol. of gelatin, no ppt.
	Tannate.	Milk-of-lime, brown color slowly formed.—Sol. of gelatin, bulky ppt.
Pale-buff ppt.	Benzoate.	See Table (A).
Pink precipitate.	Succinate.	Strong hot H_2SO_4, will not char it.

(G) To a separate portion of the original solution add a few crystals of $FeSO_4$ (and warm slightly).

Result.	Indication.	Confirmatory Tests to be Applied to Some of the Original Solution.
Black color.	Nitrite.	KI with dil. H_2SO_4 and starch paste = blue.
Black color only after adding strong H_2SO_6.	Nitrate.	KI with dil. H_2SO_4 and starch paste = no blue color.

79. **Detection of Acids in Insoluble Substances.**—Boil some of the substance in a flask for five minutes or so with a strong solution of Na_2CO_3, cool, filter, and neutralize the filtrate with HNO_3, carefully avoiding excess of the acid.

All the acid radicals of the substance will be converted

into corresponding sodium salts and dissolved in the aqueous solution. Test separate portions of this solution as under 78.

SPECIAL TESTS FOR ACIDS OF GROUP I.

(ACID BARIUM GROUP.)

1. **Sulfate.**—With $BaCl_2$ gives a white ppt. of $BaSO_4$, insoluble in acids. The solution should be acidified with HCl before adding the reagent:

$$Na_2SO_4 + BaCl_2 = BaSO_4 + 2NaCl.$$

2. **Hydrofluosilicate.**—With $BaCl_2$ gives an insoluble ppt. of $BaSiF_6$, insoluble in HCl.

With KCl gives a gelatinous ppt. of K_2SiF_6:

$$2KCl + H_2SiF_6 = K_2SiF_6 + 2HCl.$$

81. SPECIAL TESTS FOR ACIDS OF GROUP II.

(NEUTRAL BARIUM GROUP.)

4. **Phosphate.**—$BaCl_2$ produces a white ppt. of barium phosphate, soluble in HNO_3 or HCl:

$$BaCl_2 + Na_2HPO_4 = \underbrace{BaHPO_4}_{\text{Barium Phosphate.}} + 2NaCl.$$

5. $AgNO_3$ precipitates yellow silver phosphate, soluble in HNO_3:

$$3AgNO_3 + Na_2HPO_4 = \underbrace{Ag_3PO_4}_{\text{Silver Phosphate.}} + 2NaNO_3 + HNO_3.$$

6. $(NH_4)_2MoO_4$ (dissolved in HNO_3) gives a canary-yellow ppt. of ammonium phosphomolybdate easily soluble in alkalies.

7. Magnesia mixture gives a white ppt. of NH_4MgPO_4.

8. **Borate.**—Acidulate the solution with HCl, dip a piece of turmeric paper into the mixture and dry it over the gas. The paper acquires a brownish-red color, which is changed to green on moistening it with a drop of KOH.

9. Moisten the dry salt with a little H_2SO_4, or acidulate the solution, add alcohol, and ignite: a distinct green flame is produced.

10. **Oxalate.**—Heated with strong H_2SO_4, carbon monoxid, carbon dioxid, and water are produced. The CO will burn with a blue flame:

$$K_2C_2O_4 + H_2SO_4 = K_2SO_4 + CO + CO_2 + H_2O.$$

11. *With $AgNO_3$* a white ppt. of silver oxalate is producea:

$$K_2C_2O_4 + 2AgNO_3 = \underbrace{Ag_2C_2H_4}_{\text{Silver Oxalate.}} + 2KNO_3.$$

12. *With $CaCl_2$* a white ppt. of calcium oxalate is produced even with dilute solutions. The ppt. is soluble in HCl.

$$CaCl_2 + K_2C_2O_4 = \underbrace{CaC_2O_4}_{\text{Calcium Oxalate.}} + 2KCl.$$

13. **Carbonate.**—Treated with dilute acid, violent effervescence takes place, carbonic anhydrid being evolved, which produces turbidity in a drop of $Ba(OH)_2$ solution held on a glass rod near the mouth of the test-tube:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2.$$

14. **Sulfite.**—Heated with a small piece of zinc and a few drops of H_2SO_4, H_2S will be evolved, which blackens lead acetate paper.

15. With $AgNO_3$ sulfites produce a white ppt. which on being heated darkens and deposits metallic silver.

16. **Thiosulfates.**—With $BaCl_2$ produce a white ppt. of BaS_2O_3.

17. With $Pb(C_2H_3O_2)_2$ a white ppt. of lead thiosulfate is formed:

$$Na_2S_2O_3 + Pb(C_2H_3O_2)_2 = PbS_2O_3 + 2NaC_2H_3O_2.$$

18. HCl added to a solution of a thiosulphate produces a slowly forming ppt. of S and an evolution of SO_2.

19. **Arsenites.**—With $AgNO_3$ produce a yellow ppt. of Ag_3AsO_3 (silver arsenite) soluble in NH_4OH. A few drops of NH_4OH facilitate the reaction.

20. **Arsenates.**—With $AgNO_3$ produce a light-brown ppt. of $AgAsO_4$ (silver arsenate).

21. $MgSO_4 + NH_4Cl + (NH_4)HO$ produce a white ppt. of $MgNH_4AsO_4$ (distinction from arsenites).

22. **Iodates.**—With $AgNO_3$ produce a white crystalline ppt. soluble in NH_4OH:

$$2KIO_3 + 2AgNO_3 = \underbrace{2AgIO_3}_{\substack{\text{Silver}\\ \text{Iodate.}}} + 2KNO_3.$$

23. On heating, iodates are decomposed, oxygen evolved, and iodine given off in violet fumes.

24. **Chromates.**—With $BaCl_2$ form a yellow ppt. of barium chromate.

25. With $AgNO_3$ chromates give a red ppt. of silver chromate soluble in HNO_3:

$$2AgNO_3 + K_2CrO_4 = \underbrace{Ag_2CrO_4}_{\substack{\text{Silver}\\ \text{Chromate.}}} + 2KNO_3.$$

26. **Silicates.**—With $BaCl_2$ produce a white precipitate of $BaSiO_3$, which is decomposed on addition of HCl, $Si(OH)_4$ separating as a gelatinous ppt.

27. With HCl silicates are thrown out of solution as $Si(OH)_2$ = a gelatinous ppt.

82. SPECIAL TESTS FOR ACIDS OF GROUP III.

28. **Chlorids.**—Heated with H_2SO_4 and MnO_2 yield chlorin gas, recognized by its greenish color, odor, and its bleaching action on litmus and indigo.

29. With $AgNO_3$ a curdy white ppt. is obtained, sol. in NH_4OH, insol. in HNO_3.

30. **Hypochlorites.** — Heated with dilute H_2SO_4 give off chlorin, recognized by its odor; a few drops of solution KI added and *starch paste* = a blue color of starch iodid.

31. Indigo and litmus solutions acidified with dilute H_2SO_4 are decolorized.

32. Nitric acid evolves hypochlorous acid—HClO—from hypochlorites.

33. **Nitrites.**—A solution of a nitrite mixed with an equal volume of a freshly prepared solution of $FeSO_4$ is floated upon some concentrated $HC_2H_3O_2$ in a test-tube: a dark brown ring forms at line of contact. This test distinguishes nitrites from nitrates, the latter requiring H_2SO_4 to produce the brown ring.

34. The nitrite solution acidulated with dil. H_2SO_4 and some KI and starch solution added = a blue color.

35. **Sulfids.**—With $AgNO_3$ produce a black ppt. of Ag_2S.

36. With strong HCl and heat sulfids are decomposed and H_2S evolved, recognized by its odor; also, if a piece of paper moistened with $Pb(C_2H_3O_2)_2$ is held over the mouth of the test-tube, a dark coloration (PbS) results.

37. With NaOH and some sodium nitro-ferricyanid a purplish-red color is produced.

38. **Bromids.**—With $AgNO_3$ produce a pale-yellow ppt. of AgBr, insoluble in dilute HNO_3, but readily soluble in $Na_2S_2O_3$:

$$KBr + AgNO_3 = AgBr + KNO_3.$$

39. With chlorin water the solution is colored through the liberation of bromin; add a few drops of chloroform to the solution and shake; the chloroform will carry to the bottom the dissolved Br as a golden-yellow solution:

$$KBr + Cl = KCl + Br.$$

40. Liberate Br as in preceding test and add starch paste; the orange coloration is due to the formation of starch bromid.

41. **Bromates.**—With dilute H_2SO_3 liberate Br; add starch paste and orange-colored starch bromid will form:

$$2KBrO_3 + 5H_2SO_3 = 3H_2SO_4 + 2KHSO_4 + H_2O + Br.$$

42. **Iodids.**—With solutions of $CuSO_4$ acidified with H_2SO_4 produce a dirty-white ppt. of Cu_2I_2 (distinction from bromids and chlorids).

43. Liberate I as in test 39, or by the addition of strong H_2SO_4, add chloroform, and shake: it will dissolve in the chloroform and be carried to the bottom as a purple-colored solution.

44. Liberate iodin as in 39, add starch paste = characteristic blue color of starch iodid.

45. **Cyanids.**—Prepare a mixture of solutions of $FeSO_4$ and Fe_2Cl_6, add NaOH and a few drops of HCl, then a solution of a cyanid: a blue ppt. Prussian blue will develop.

(1) $2KCy + FeSO_4 = Fe(Cy)_2 + K_2SO_4.$
(2) $4KCy + Fe(Cy)_2 = K_4FeCy_6.$
(3) $3K_4FeCy_6 + 2Fe_2Cl_6 = Fe_4(FeCy_6)_3 + 12KCl.$

46. Heated with a few drops of dil. H_2SO_4, cyanids decompose, evolving HCy, recognized by the odor of bitter almonds:

$$2KCy + H_2SO_4 = K_2SO_4 + 2HCy.$$

(*Caution!* The gas so evolved should be cautiously sniffed, it being highly poisonous.)

47. **Cyanates.**—With HCl in presence of H_2O form cyanic acid and corresponding Cl salts; heating this splits the acid and the chlorid into $NH_4Cl + CO_2$, for both of which test with appropriate reagents.

48. **Chlorate, Bromate, and Iodate.**—These salts, in the dry state, when heated evolve oxygen and are reduced to chlorid, bromid, and iodid respectively. Hence if the salt deflagrates when heated with charcoal, heat another portion on porcelain and test portions of the residue for chlorids, bromids, and iodids with appropriate reagents.

49. **Chlorids, Bromids, and Iodids.**—In mixtures these are separated and identified as follows: Place a small quantity of the mixture in a test-tube, add a few grains MnO_2 (free from chlorids) and a drop of dilute H_2SO_4, and boil. If violet vapors are evolved = *iodid.* Add 2 more drops of the acid and boil again until all the I is volatilized. Now add about 30 drops more of H_2SO_4 and boil. If brown vapors are given off = *bromid.* Boil until all the Br is volatilized, then allow to cool. To the residue add an equal bulk of concentrated H_2SO_4 and warm. If a green gas is evolved (with an odor of Cl) = *chlorid.* Apply the bleaching test as in 28.

83. SPECIAL TESTS FOR ACIDS OF GROUP IV.

50. **Nitrates.**—Upon being heated evolve oxygen; if acidified with H_2SO_4 and heated they are decomposed into NO_2 and H_2O with the evolution of oxygen.

51. When heated on charcoal they deflagrate violently.

52. A solution of a nitrate mixed with an equal volume of freshly prepared $FeSO_4$ sol. and floated on H_2SO_4 = a brown ring at line of contact.

53. **Chlorates.**—When heated are decomposed into chlorids as described in 48 and are similarly tested for.

54. Strong HCl decomposes chlorates with evolution of Cl and Cl_2O_4 mixture, known as "euchlor" or *euchlorin.*

55. **Perchlorates.**—In the dry state evolve oxygen on being heated.

56. **Sulfocyanates.**—Heated with dilute H_2SO_4 give off HCy (see Caution in 46) and a ppt. of S forms.

57. With $CuSO_4$ sulfocyanates produce a black crystalline ppt., which changes to white on the addition of $FeSO_4$.

58. With Fe_2Cl_6 a blood-red solution is produced.

59. **Ferrocyanids.**—With $CuSO_4$ produce a brownish-red ppt., Cu_2FeCy_6:

$$K_4FeCy_6 + 2CuSO_4 = Cu_2FeCy_6 + 2K_2SO_4.$$

60. With $AgNO_3$ a white ppt. of Ag_4FeCy_6 is formed:

$$K_4FeCy_6 + 4AgNO_3 = Ag_4FeCy_6 + 4KNO_3.$$

61. With Fe_2Cl_6 = a deep-blue ppt.

62. **Ferricyanids.**—With $AgNO_3$ produce an orange-colored ppt. of $Ag_6\ (FeCy_6)_{12}$, insoluble in HNO_3, but soluble in KCy:

$$K_6(FeCy)_{12} + 6AgNO_3 = Ag_6(FeCy)_{12} + 6KNO_3.$$

63. With $FeSO_4$ = a blue ppt.

64. **Hypophosphites.**—When the dry salt is heated in a test-tube, PH_3 is given off, which bursts into flame.

65. With $AgNO_3$ a white ppt. forms which quickly turns brown.

66. In acidulated solutions $HgCl_2$ gives white ppt., which on heating turns black.

67. **Carbonates and Bicarbonates.**—Both effervesce when H_2SO_4 is added, giving off a colorless gas.

68. $HgCl_2$ produces a red ppt. = carbonate; $HgCl_2$ produces a white ppt. = bicarbonate.

84. SPECIAL TESTS FOR ORGANIC ACIDS.

69. **Acetates.**—Heated with strong H_2SO_4 give off acetic acid, recognized by its strong odor of vinegar:

$$NaC_2H_3O_2 + H_2SO_4 = NaHSO_4 + CH_3COOH$$

70. Heated with alcohol in presence of strong H_2SO_4 acetic ether is evolved:

$$NaC_2H_3O_2 + C_2H_5OH + H_2SO_4 = CH_3COOC_2H_5 + NaHSO_4 + H_2O.$$

71. With Fe_2Cl_6 = a red-colored solution of $Fe_2(C_2H_3O_2)_6$, to which add HCl: the red color is discharged (distinction from sulfocyanids).

72. **Citrates.**—Heated in a test-tube char slowly, emitting a weak odor of burnt sugar:

$$2K_3C_6H_5O_7 = 3K_2CO_3 + 5H_2O + C_9.$$

73. With $CaCl_2$ citrates yield, on boiling, a white ppt. of $Ca_3(C_6H_5O_7)_2$:

$$2K_3C_6H_5O_7 + 3CaCl_2 = Ca_3(C_6H_5O_7)_2 + 6KCl.$$

74. **Tartrates.**—Heated in a dry test-tube char rapidly (difference from citrates), evolving CO (test as in 10) and a strong odor of burnt sugar:

$$K_2C_4H_4O_6 = K_2CO_3 + C_2 + CO + 2H_2O.$$

75. With $CaCl_2$ a white precipitate, $CaC_4H_4O_6$, forms on shaking, without heating (distinction from citrates).

Wash the above ppt. with H_2O, and add KOH: it dissolves (distinction from citrates).

76. The solution warmed with $AgNO_3$ and a few drops of NH_4OH = a silver mirror.

77. **Benzoates.**—With HCl a flocculent ppt. of benzoic acid forms:

$$NH_4C_7H_5O_2 + HCl = HC_7H_5O_2 + NH_4Cl$$

(distinction from succinate, the latter not ppt'g with HCl).

78. Heat some dry salt with twice its weight of $Ca(OH)_2$: benzene is evolved:

$$(1)\ 2NH_4C_7H_5O_2 + Ca(OH)_2 = Ca(C_7H_5O_2)_2 + 2NH_3 + 2H_2O.$$

$$(2)\ Ca(C_7H_5O_2)_2 + H_2O = \underbrace{2C_6H_6}_{\text{Benzene.}} + CaCO_3 + CO_2.$$

79. With Fe_2Cl_6 = a light buff-colored ppt.

80. **Salicylates.**—Heated in a dry test-tube decompose into phenol, CO_2, and carbonate:

$$2NaC_7H_5O_3 + H_2O = Na_2CO_3 + \underbrace{2C_6H_5OH}_{\text{Phenol.}} + CO_2.$$

81. With Fe_2Cl_6 = a violet-colored ppt. of ferric salicylate, $Fe_2(C_7H_5O_3)_6$:

$$6NaC_7H_5O_3 + Fe_2Cl_6 = Fe_2(C_7H_5O_3)_6 + 6NaCl.$$

82. **Formates.**—Heated in the dry state with strong H_2SO_4 does not char, but evolves CO and H_2O. (Test for CO by 9.)

$$NaCHO_2 + H_2SO_4 = NaHSO_4 + CO + H_2O.$$

The fact that it does not char distinguishes it from all other organic acids commonly met with, except oxalic acid.

83. With Fe_2Cl_6 = a red coloration, discharged by HCl (distinction from sulfocyanids).

84. With $AgNO_3$ in presence of $HC_2H_3O_2$, on boiling, formates deposit a silver mirror on the side of the tube (distinction from acetate):

(1) $NaCHO_2 + AgNO_3 = AgCHO_2 + NaNO_3$.
(2) $2AgCHO_2 = Ag_2 + H_2O + CO + CO_2$.

85. **Lactates.**—Heated with excess of strong H_2SO_4 give off a large quantity of CO. (There are no characteristic tests for lactates.) Heated with dilute H_2SO_4 lactates yield acetaldehyd and formic acid:

$$\begin{array}{lclcl} CH_3 & & & & \\ \vert & & & & \\ CH.OH & = & CH_3 & & H \\ \vert & & \vert & + & \vert \\ COOH & & COH & & COOH \end{array}$$

86. **Molybdates.**—Heated with water in presence of alcohol and a drop of H_2SO_4, blue color is produced.

87. Heated with solutions of Na_2HPO_4 and NaOH in presence of HNO_3, a canary-yellow ppt. of molybdenum-ammonium phosphate falls.

88. **Tannates, or Tannin.**—With Fe_2Cl_6 = a blue-black ppt. of ferric tannate (ink).

89. **Gallates, or Gallol.**—With Fe_2Cl_6 = a blue-black ppt. soluble in excess to a green solution (distinction from tannates).

90. **Pyrogallates, or Pyrogallol.**—With Fe_2Cl_6 = a red coloration discharged by HCl.

91. **Valerates.**—Heated in a dry test-tube evolve valeric acid, leaving a residue of a carbonate.

92. **Meconates.**—With a neutral Fe_2Cl_6, solutions of a meconate give a red solution of iron meconate, $Fe_2(C_7H_4O_7)_2$. Divide the solution into two parts, *a* and *b*.

To (*a*) add $HgCl_2$: the color remains.
To (*b*) " HCl: the color is not discharged.

(This reaction is used in testing for opium or its preparations.)

Acetates and sulphocyanates give the same red color, but that produced by acetates is discharged by both HCl and $HgCl_2$, while the color produced by sulphocyanates with Fe_2Cl_6 is discharged by $HgCl_2$ only.

93. **Phenolates, also called Carbolates.**—When treated with Fe_2Cl_6 give a reddish-violet color similar to that produced with salicylates.

Heated with strong H_2SO_4, an odor of phenol is evolved:

$$NaC_6H_5O + H_2SO_4 = NaHSO_4 + C_6H_5OH.$$

(Distinction from salicylates.)

PART III.

QUALITATIVE ANALYSIS OF ORGANIC SUBSTANCES.

85. If a substance chars when heated on platinum foil, or burns with evolution of carbon dioxid, its organic nature is established.

The Procedure for the Detection of the Ultimate Constituents of Organic Substances is as follows:

(1) *Carbon* and *Hydrogen.*—Mix a small quantity of the substance with about six times its bulk of freshly ignited and powdered cupric oxid, place the mixture in a small test-tube and cover it with a layer of cupric oxid. Then close the tube securely with a cork bearing a delivery-tube bent twice at right angles, and apply heat. (*a*) Gas is evolved (CO_2). The gas is passed into a clear solution of $Ba(OH)_2$. If the solution becomes turbid (through formation of $BaCO_3$), carbon is indicated. (*b*) If drops of water or moisture are deposited in the upper, cold part of the tube, hydrogen is indicated.

(2) *Nitrogen.*—If a substance when heated on platinum emits an odor of burnt hair or horn, nitrogen is indicated.

The presence of nitrogen is, however, more accurately determined as follows: Mix about 2 gm. of the substance with 4 gm. of dried powdered soda-lime, and heat. If nitrogen is present, there will be observed an odor of NH_3, recognized also by its turning red litmus blue, and by its forming white fumes when a glass rod moistened with HCl is brought near the mouth of the tube.

(3) *Chlorin.*—The presence of the halogens in most organic

compounds cannot be detected by the simple addition of silver nitrate; therefore a method similar to the following must be employed:

Mix 1 gm. of the substance with 2 gm. of pure CaO in a test-tube and heat to redness. Then dissolve the residue in distilled water strongly acidulated with HNO_3, filter, and test for chlorin with $AgNO_3$. In this process the CaO is converted into $CaCl_2$.

(4) *Sulfur.*—(In Solids.) Mix 1 gm. of the substance with 1 gm. each of KNO_3 and KOH and subject the mixture to fusion. The sulfur is oxidized, and converted into K_2SO_4. The fused mass is then dissolved in distilled water, acidified with HCl, and tested with $BaCl_2$. A white ppt. ($BaSO_4$) indicates sulfur.

(In Liquids.) Sulfur is detected by heating 3 cc. of the liquid with strong HNO_3. This converts the sulfur into H_2SO_4, which, after diluting with water, is tested with $BaCl_2$.

(5) *Phosphorus* may be detected as described above (for sulfur in solids). The fusion converts phosphorus into H_3PO_4. The fused mass is dissolved in water and tested for phosphate with magnesia mixture.

Another way is to heat about 2 gm. of the substance with HNO_3, dilute with water, filter, and test separate portions of the filtrate with, first, Fe_2Cl_6 in presence of sodium acetate = a brown ppt.; and, second, ammonium molybdate solution = a yellow ppt.

86. BEHAVIOR OF ORGANIC SUBSTANCES WITH IMMISCIBLE SOLVENTS.

Upon agitating the substance with distilled water acidulated with 2% of H_2SO_4, and adding half its volume of an immiscible solvent (ether, chloroform, or benzene) the following are extracted:

(1) In the *Acidulated Aqueous Liquid* there may be dissolved *carbohydrates, soluble alkaloidal salts, acids, organic bases, and*

proteids. Add a small excess of NaOH solution and half its volume of an immiscible solvent and again shake, thus further separating the above into (*a*) and (*b*).

(*a*) *The Alkaline Aqueous extract may contain:*

Carbohydrates; as, dextrin, sugars, gums.

Soluble Alcohols; as, methyl, ethyl, propenyl.

Soluble Acids; as, acetic, tartaric, citric, lactic, malic, oxalic.

Alkaloids and Organic Bases; as, urea, curarine, cinchonine, pyridine, and morphine.

Coloring matters; as, indigo, cochineal, cudbear.

Proteids; as, albumin, casein, gelatin.

(*b*) *The Immiscible layer may contain:*

Vegetable Alkaloids; as, quinine, strychnine, aconitine, atropine, nicotine.

Coal-tar Bases; as, aniline, chrysotoluidine, pyridine, and their homologues.

(2) *In the Immiscible Solvent* there may be dissolved *hydrocarbons, oils, acids, coloring matters, resins, phenols, and glucoids.* Add water containing a small excess of NaOH and shake again, thus further separating the above into (*a*) and (*b*).

(*a*) *The Alkaline Aqueous Extract may contain:*

Fatty acids; as, stearic, oleic, palmitic, valeric.

Aromatic acids; as, benzoic, salicylic, phthalic.

Acid coloring matters and dyes; as, picric or chrysophanic acid; aurin, saffranin, alizarin, or bilirubin.

Acid Resins; as, colophony (common pitches).

Phenols; as, phenic and cresylic acids; thymol and creosote.

Glucosids; as, santonin, picrotoxin.

(*b*) *The Immiscible layer may contain:*

Hydrocarbons, solid; as, paraffin, napthhalene, anthracene.

Hydrocarbons, liquid; as, petroleum products, rosin-oil, benzene.

Essential oils; as, turpentine, terpene, and oxygenated oils.

Nitro-compounds; as, nitro-benzene.

Chloroform, also Ethers; as, ethyl oxid, ethyl acetate, etc.; nitro-glycerin.

Fixed fats, oils, and waxes.

Neutral resins and coloring matters.

Camphors; as, laurel-camphor, borneol, menthol.

Insoluble Alcohols; as, amyl, cetyl, and cholesterin.

Glucosids; as, saponin, santonin, and digitalin.

Weak Alkaloids; as, caffeine, narcotine, piperine, colchicine.

87. BEHAVIOR OF ORGANIC SUBSTANCES WITH FEHLING'S SOLUTION.

The substance should be made perfectly neutral and brought into solution. One cc. of the solution is heated with 10 cc. of Fehling's Reagent to boiling. In some cases the reduction occurs in the cold or on gently heating the liquid. A yellow or orange-red precipitate or turbidity caused by the precipitation of cuprous oxid (Cu_2O) indicates reducing substance, thus:

Fehling's Reagent is Reduced by	Fehling's Reagent is Not Affected by
Carbohydrates. — Lactose, dextrose, laevulose, maltose, mannitose, arabinose, galactose.	*Carbohydrates.*—Mannite, saccharose, dulcite, cellulose, dextrin, arabin.
Alcohols and Phenols.—Aldehyd, chloral, chloroform, valeric aldehyd, resorcinol.	*Alcohols and Phenols.*—Alcohol, glycerin, phenol, benzoic and salicylic aldehyds.
Organic Acids.—Pyrogallic, gallotannic, trichloracetic.	*Organic Acids.*—Acetic, oxalic, succinic, lactic, tartaric, citric, gallic, mucic, benzoic, and salicylic.
Inorganic Acids.—Arsenous.	*Inorganic Acids.*—Sulfurous, etc.

88. A SYSTEMATIC SCHEME FOR THE IDENTIFICATION OF THE MOST IMPORTANT CARBOHYDRATES.*

STEP 1.—General reaction.

To 5 cc. of a weak solution of the substance add a few drops of 15 per cent alcoholic solution of alphanaphthol, and overlay this on strong sulphuric acid; a violet or blue zone at the line of contact indicates *a carbohydrate.*

If the substance is insoluble in water, dissolve in 25-per cent. sulfuric acid and float over this solution a mixture of water and alphanaphthol, and observe as above.

STEP 2.—Shake about 1 grm. of the substance with 10 cc. of water in a test-tube. Decant or filter from any insoluble residue, which may be starch or cellulose. Save the filtrate for the succeeding steps, and test the residue as follows:

To the insoluble matter in the test-tube (not on the filter-paper) add a few drops of a dilute aqueous solution of iodin; a blue color indicates *starch.*

STEP 3.—Take a portion of the filtrate obtained in step 2 and divide into two parts.

To one part add an equal volume of strong alcohol; a precipitate indicates *dextrin.*

To the other part on a white slab add a few drops of dilute solution of iodin; a blue color indicates *cooked starch,* and a reddish-brown color, *dextrin.*

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* E. H. Bartley's Clinical Chemistry, p. 17.

89. CHART FOR THE DETECTION OF THE MORE COMMON ORGANIC COMPOUNDS OF PHARMACEUTICAL INTEREST.

Dissolve a small quantity of the dry substance in a little dilute HCl, and add a drop or two of potassio-bismuthic iodid solution. If a reddish-brown ppt. forms, an alkaloid is indicated. Apply Step I. If no ppt. forms, pass on to Step V and then to Step VI.

STEP I.—To drop of HNO_3 on a white porcelain tile add a small quantity of the substance and observe the color.

Red *changing to yellow* = **Morphine.** Fröhde's Reagent gives a purple color. Sulphuric acid containing a crystal of KIO_3 = a dark brown. A few drops of Fe_2Cl_6 sol. added to a neutral solution (1:100) of morphine = a blue color destroyed by acids. Sulphuric acid containing in each cc. 1 drop of sol. of formaldehyde gives with morphine an intense purple color.	**Red = Brucine.** Color changes to purple on addition of a drop of $Na_2S_2O_3$ solution. To crystal of the alkaloid add chlorin-water = an evanescent rose-red. To another crystal add HNO_3, then some solution of $AgNO_3$, and warm = a carmine-red. To another crystal add bromin-water = a yellow ppt. and forming a red sol. on warming.
Yellow *changing to* **Red** *on heating* = **Physostigmine.** With H_2SO_4 Physostigmine yields a faint yellow color. With H_2SO_4 containing a crystal of KIO_3 = a purple color changing to yellowish red. KOH added to the aqueous sol. yields a white ppt. which quickly turns pink soluble in excess to a pink or red sol.	**Reddish Brown = Aconitine.** With H_2SO_4 containing a crystal of ammonium vanadate = orange color. With H_2SO_4 and a grain or two of sugar = red color. With H_2SO_4 on gently warming = violet color. With Fröhde's Reagent = a yellow-brown color.
Red Crystals *with yellow-colored solution* = **Codeine.** With H_2SO_4 and warming = a violet color. With H_2SO_4 and a trace of $FeCl_6$ = a violet-blue color. With H_2SO_4 containing a little HNO_3 upon heating gives a blood-red color.	**Purple** *fading to orange* = **Apomorphine.** With H_2SO_4 and a trace of Fe_2Cl_6 = a pale blue. With H_2SO_4 containing a trace of HNO_3 = a blood-red color. With H_2SO_4 containing a little paraldehyde = a green color fading to reddish brown. Dilute Fe_2Cl_6 sol. colors the alkaloid solution red.

STEP II.—Cover a few grains of the alkaloid with a drop or two of conc. H_2SO_4 on a white porcelain tile, and add a small fragment of potassium dichromate. Observe effect.

Deep Blue	Green
quickly changing to violet, purple, cherry-red and finally to orange = Strychnine. With H_2SO_4 containing a trace of ammonium vanadate = a violet-blue, gradually changing to cherry-red. With H_2SO_4 containing a trace of KIO_3 = a violet color, changing to purple. (See also Acetanilide.)	*color slowly formed* = Caffeine. If a small quantity of salt be dissolved in 1 cc. of HCl and a little $KClO_3$, and the sol. evaporated to dryness, the residue, subjected to the vapor of ammonia, will acquire a rich purple color. (See also Cinchonidine.)
Odor *of bitter almonds* = Atropine. Heated with a few cc. of H_2SO_4 = a peculiar odor, resembling a mixture of rose, orange flower and melilot. The addition of a crystal of $K_2Cr_2O_7$ develops an odor of bitter almonds. With AuCl a yellow lusterless ppt. is produced in a HCl solution of atropine.	Pale Yellowish Pink = Cocaine. If 5 drops of CrO_3 sol. (1:20) be added to 5 cc. of cocaine sol. = a yellow ppt., dissolved on shaking. On now adding 1 cc. of HCl an orange-colored ppt. is produced. Its solution in HCl gives with K_2CrO_4 sol. an orange ppt. With $KMnO_4$ sol. a violet ppt. is produced.

STEP III.—To a fragment of the alkaloid on a porcelain crucible cover add a few drops of conc. HCl and warm.

A Rose-red color = Veratrine.

Confirmatory tests:

Heated with H_2SO_4 = a cherry-red color.

With H_2SO_4 and sugar = a green changing to blue.

With HNO_3 = a yellow color.

With Fröhde's reagent = a cherry-red.

(See also Physostigmine.)

STEP IV.—Heat a little of the original in a dry test-tube. Vapors are evolved, first yellow then red = **cinchona alkaloids,** Take another small portion of the alkaloid, dissolve it in water with the aid of the least quantity of dilute H_2SO_4, then add some bromine-water, and a slight excess of ammonia-water. *An* **Emerald Green** *Color* indicates **Quinine** or **Quinidine**; a white ppt. may indicate **Cinchonine** or **Cinchonidin.** Apply the following tests:

REAGENT.	Quinine.	Quinidine.
A 1% solution of the alkaloid, made by using the smallest possible quantity of dil. H_2SO_4 and neutralized with NH_4OH, is treated with one drop of H_2O_2 and one drop of $CuSO_4$ sol. and boiled.	Intense *red* color changing to blue and green.	Intense *red* color changing to blue and green.
Dissolve a small quantity of the alkaloid in a mixture of acetic acid and alcohol with a few drops of H_2SO_4, boil, and add tr. iodin slowly.	Bronze or olive-green crystals separate on cooling. (Quinine-iodosulphate.)	No ppt. or crystals.
To a neutral aqueous solution add $(NH_4)_2C_2O_4$ or $KNaC_4H_4O_6$ sol.	White ppt.	Precipitate only on addition of KI and shaking.
Fröhde's Reagent.	Green color.	Green color.

REAGENT.	Cinchonin.	Cinchonidin.
Make a nearly neutral solution of the alkaloid. Add some sat. sol. of $KNaC_4H_4O_6$.	No white ppt. unless excess of NH_4OH is added.	A white ppt.
Make a solution of the alkaloid in $HC_2H_3O_2$. Add some NH_4OH, and then an excess of ether.	The ppt. does not dissolve in the ether.	The ppt. dissolves in the ether.

STEP V.—If the substance is not an alkaloid, place a small portion of it on a porcelain crucible cover, add a drop or two of Fröhde's Reagent and observe the color changes.

Salicin.	Santonin.
Intense violet color changing to reddish brown. With H_2SO_4 = a bright-red color which disappears on the addition of water. To some of the substance add dilute sulfuric acid and a crystal of $K_2Cr_2O_7$ and boil = odor of sweet clover (salicylic aldehyd). On heating a portion of the substance in a test-tube until it turns brown, then adding water and a drop of Fe_2Cl_6 sol. = a violet color.	Slate-blue color on warming. Add a drop of Fe_2Cl_6 to some H_2SO_4, warm, and add some of the substance = a violet-red color changing to brown. On heating a portion of the substance with alcoholic KOH sol. = a red color. The substance is soluble in NaOH, reprecipitated by acids.

Elaterin.	Aloin.
Faint red changing to olive-green on warming. Add a drop of phenol, then a drop of H_2SO_4, to some of the substance, and warm = a rose-red color. With H_2SO_4 = a yellow color changing to red. With H_2SO_4 + a drop of formaldehyde = a brown color. With H_2SO_4 + a trace of ammonium vanadate = a blue, changing to green and brown.	Yellow color changing to green. Ammonia-water and alkali sols. dissolve aloin forming a yellow sol. quickly turning red. With conc. H_2SO_4 + a crystal of $K_2Cr_2O_7$ = an olive-green, and finally, on standing, a blue color. With bromine-water = a pink color. With $AuCl_3$ in an aqueous solution = a carmine-red changing to violet. With a drop of Fe_2Cl_6 sol. its alcoholic sol. gives a brownish-green color. HNO_3 gives with barbaloin a crimson, with nataloin a red, and with socaloin a brown, ppt.

STEP VI.—Heat some of the substance in a dry test-tube and observe odor or other effect.

(*a*) **Odor of Phenol** indicates:

Phenol (see 162).

Phenolates (par. 78, Tables A and F), or

Phenolsulphonates (par. 78, Tables A and F).

(*b*) **Odor** is **Pungent**; may be *Chloral, Benzoic Acid, Benzoates,* or *Butyl Chloral.*

Chloral.	Benzoic Acid or Benzoates.	Butyl Chloral.
Heated with KOH or NH_4OH an odor of chloroform is evolved and a formate of the base is produced. Warmed with a few drops of aniline and some KOH = a very disagreeable odor of phenyl-isocyanide. Warmed with a few drops of NH_4OH and a little $AgNO_3$ sol. = a silver mirror. Boiled with Fehling's sol. = a red ppt.	Upon heating benzoic acid with freshly slaked lime in a dry test-tube *benzene* (benzol) is evolved. A sol. of benzoic acid in NaOH neutralized carefully gives with neutral ferric chloride sol. a pale buff or flesh-colored ppt. *See* par. 78, Tables A and F, also par. 84, No. 77, for tests for benzoates.	Sparingly soluble in water. Boil with NaOH, neutralize with dilute $HC_2H_3O_2$ and add $AgNO_3$ sol. = a white ppt.

(*c*) **Odor** is **Pungent**; with **Iodin Fumes** indicates *Iodoform, Iodol,* or *Aristol.*

Iodoform.	Iodol.	Aristol.
A *yellow* insol. powder. When boiled with NaOH and the sol. neutralized with HNO_3 = a yellow ppt. on adding $AgNO_3$ sol., and a *blue* color on adding starch sol.	A *grayish-brown* powder very sparingly soluble in water. When dissolved in conc. H_2SO_4 a green sol. results gradually changing to brown.	A *bright chocolate-colored* powder, with an aromatic odor. It is not sol. in alkaline hydroxid solutions. Heated with conc. H_2SO_4 it decomposes, and iodine separates.

(*d*) **Odor is Camphoraceous**; may be *Camphor, Thymol,* or *Menthol.*

Camphor.	Thymol.	Menthol.
Soluble in the volatile solvents, and in fixed oils. Its alcoholic solution poured into cold water = a curdy white ppt. When triturated with hydrated chloral liquefaction ensues. It is inflammable and burns with a luminous, smoky flame.	An aromatic thyme-like odor. Soluble in ether, chloroform, alcohol, and oils, also in glacial acetic acid. Its sol. in the latter when treated with H_2SO_4 and a drop of HNO_3 exhibits a bluish-green color by reflected light. If heated with NaOH sol. in a test-tube a pale-red sol. is formed which becomes darker on standing. A few drops of chloroform added gives a violet color.	Soluble in alcohol, chloroform and ether. It has a peppermint-like odor. It is soluble in glacial acetic acid, but does not respond to the test for thymol. Heated with diluted sulfuric acid 1 : 2 = a deep-blue color.

(*e*) **Odor is Acrylic** (Fatty Acid); indicates *Soap, Oleates,* or *Stearates.*

Soap.—Dissolve in water, add HCl and shake, add some ether and again shake; then let the mixture stand so that the ethereal layer can separate; remove the upper layer and evaporate: the residue if liquid is oleic, and if solid, stearic acid. The HCl sol. is evaporated to dryness and tested for K and for Na.

Oleates and **Stearates** of the heavy metals are treated in the same way. The acid sol. residue being tested for the metals commonly combined with these fatty acids, i.e., Zn, Pb, Hg, etc.

(*f*) **Odor** resembling **Burnt Bones**; may indicate **Oxgall.**

To a warm aqueous solution of oxgall add a crystal of sugar; shake, and add H_2SO_4 cautiously until the ppt. first formed is redissolved; a brownish-red color gradually develops, changing to carmine, purple, and violet.

(*g*) **Odor of Burning Sugar;** may be *Sugars, Dextrin, Starches, Gums, Tartaric Acid or Tartrates.* Apply special tests. For tartrates, see par. 84, No. 74. For the sugars, see the Table below; also see Scheme in par. 88 for other carbohydrates.

Cane-sugar.	Milk-sugar.
Strong H_2SO_4 chars it immediately. Does not reduce Fehling's sol. Mixed dry with $KClO_3$ crystals and a drop of conc. H_2SO_4 added, it deflagrates. It does not ferment with yeast until left in contact for some time. Boiled with $NaOH$ = no effect. It does not form a compound with phenylhydrazine.	Strong H_2SO_4 chars it slowly. It reduces Fehling's sol. It does not ferment with yeast. It combines with phenylhydrazine to form phenyl-lactosazone in acetic acid solutions. Boiled with $NaOH$ = no effect.

Grape-sugar.	Dextrin.
Strong H_2SO_4 does not char it until heated. It readily reduces Fehling's sol. It also reduces alkaline solutions of Bi, Ag, and Hg. In a solution acidified by $HC_2H_3O_2$ it forms, with excess of phenylhydrazine, a yellow ppt. of phenyldextrosazone. It ferments readily upon adding yeast to its solution. Boiled with $NaOH$ = a deep-brown color.	Strong H_2SO_4 = no effect. In aqueous sol. reduces Fehling's sol. only after long boiling. Boiled with $NaOH$ = no effect.

Starches. Insoluble in cold water, but on boiling it forms a mucilage, which gives a blue color with iodin.

Boiled with dilute sulfuric acid, it is converted into dextrose, and then reduces Fehling's sol.

Gums. Soluble in cold water, from which sol. it is precipitated by alcohol, borax or lead-acetate solution.

Gum arabic is an arabate of calcium. Ignite some of it, dissolve the ash in dilute acetic acid and test for Ca, with $(NH_4)_2C_2O_4$.

(*h*) **If detonation occurs,** it indicates **Picric Acid.** Dissolve a little of the substance in NaOH sol., add a little sugar, and warm the mixture = a blood-red color.

To an aqueous solution add a solution of gelatin = a white ppt.

Its aqueous sol. precipitates albumin, and gives a green ppt. with ammonio-copper sulfate.

(*i*) **If it burns with a smoky flame,** it may be resin.

Resin. Insoluble colored substance. A small piece of it treated with strong H_2SO_4 gives a red coloration; add a drop of H_2O to this = balsamic, turpentiny odor.

Guaiacum Resin. Insoluble colored substance. Dissolved in alcohol and treated with Fe_2Cl_6, gives a blue coloration. A small piece of it treated with strong H_2SO_4 for a few seconds, then water added, gives a characteristic balsamic odor.

(*j*) **If it at first melts and then upon highly heating burns away entirely,** it may be *acetanilide, antipyrine, phenacetin, saccharin, naphthalene,* or *urethane.*

Acetanilide: 1 grm. of acetanilde heated with 5 cc. of conc. sol. of KOH, and 1 cc. of chloroform added = a disagreeable odor of phenyl isocyanide (dist. from antipyrine and exalgine).

0.1 grm. boiled with 2 cc. HCl and 3 cc. of phenol sol. (1: 20) and then mixed with 5 cc. of a clear sol. of chlorinated lime = a brownish-red color, becoming blue upon supersaturating with NH_4OH.

1 grm. heated with 10 cc. of water, the sol. cooled and filtered and treated with bromin-water drop by drop gives a whitish ppt. of parabromoacetanilide.

Antipyrine, *Phenazonum, Phenyldimethylisopyrazolon.*—If .1 grm. of $NaNO_2$ and 12 cc. of 1% sol. of antipyrine be mixed and 1 cc. of dil. H_2SO_4 added, a deep-green color (iso-nitrosoantipyrine) develops.

A sol. of antipyrine (1: 1000) treated with 1 drop of Fe_2Cl_6

sol. = a deep-red color, which is turned yellow by H_2SO_4.

Tannic acid sol. gives a white ppt.

HNO_3 produces a red coloration.

Phenacetin, *Acetphenetidin.*—HNO_3 produces a yellow color which persists on heating.

Boiled with conc. HCl, the solution diluted with water, cooled and filtered, and then 3 drops of sol. of CrO_3 (1:30) added, a ruby-red color is produced.

Fe_2Cl_6 sol. produces a yellow solution, which becomes blood-red on boiling.

Saccharin, *Glusidum, Benzosulfinid.*—It has an intensely sweet taste. It is soluble in alkali solutions and in $NaHCO_3$ sol. with evolution of CO_2. If subjected to a high temperature it melts and finally burns, giving off an odor of essential oil of bitter almonds.

Heated to redness with Na_2CO_3 it chars and gives off an odor of benzene.

Its solution in $NaHCO_3$, neutralized with HCl, gives with Fe_2Cl_6 a reddish-brown color.

Naphthalene.—It melts and volatilizes; its vapor is inflammable, burning with a luminous smoky flame.

It may be recognized by its characteristic odor, resembling that of coal-tar.

It is insol. in water but sol. in the volatile solvents.

Urethane, *Ethyl Carbamate.*—When heated it melts, when highly heated it is decomposed, burning without leaving a residue.

A small quantity added to H_2SO_4 and gently heated is decomposed, with evolution of CO_2, while alcohol and NH_4HSO_4 remain in sol.

When heated with conc. sol. KOH ammonia is given off.

If a little be dissolved in water together with some Na_2CO_3 and a minute quantity of iodin and warmed, yellow crystals of iodoform are produced.

(*k*) **If it at first melts and at red heat is decomposed without burning** it may be (1), if without odor, *Chloralformamide;* (2) if with odor of SO_2, *Sulfonal* or *Trional.*

Chloralformamide, *Chloralamide.*—It is soluble in water. It is not affected by dilute acids.

Its solution is decomposed when warmed with KOH; it becomes turbid, then clear, and gives off chloroform.

Sulfonal, *Sulfomethane, Diethylsulfondimethylmethane.*—Slightly sol. in cold, readily in hot water. When heated it melts. At a red heat it is consumed and SO_2 is evolved.

When heated with an equal weight of powdered charcoal, the disagreeable odor of mercaptan is developed.

When heated with dry $NaC_2H_3O_2$, gaseous H_2S is evolved.

Trional, *Sulfonethylmethane.*—The tests for trional are the same as those described for sulfonal.

It differs in solubility, being soluble in 195 parts of water at 77° F. while sulfonal requires 360 parts of water. It is also more soluble in ether and in alcohol than sulfonal. Trional has a bitter taste; sulfonal is tasteless.

(*l*) **If it at first melts and finally upon increasing the heat volatilizes or sublimes,** it may be *Resorcinol, Camphor Monobromated, Guaiacol Carbonate;* and if it has a phenol-like odor, *Betanaphthol,* or if an aromatic odor, *Salol, Guaiacol,* or *Terpin Hydrate.*

Resorcinol, *Resorcin.*—It is very sol. in water, alcohol, ether and glycerin, slightly sol. in chloroform and in CS_2.

Its aqueous solution treated with a few drops of Fe_2Cl_6 sol. = a bluish color, changing to brownish-yellow on adding NH_4OH.

A small quantity heated with KOH sol. and a drop of chloroform gives a bright red color (due to formation

of rosolic acid). The addition to this of a slight excess of HCl changes the color to pale yellow.

On heating a fragment with a grain of tartaric acid, and 10 drops of H_2SO_4, a thick red liquid results, which becomes pale yellow when diluted with water.

Camphor Monobromated.—Almost insol. in water, freely sol. in volatile solvents and in cold conc. H_2SO_4.

When heated it melts and sublimes.

If a few crystals are fused in a dry test-tube with metallic Na, the residue dissolved in water and acidulated with HNO_3 gives with $AgNO_3$ sol. a copious white ppt.

It has a camphoraceous odor and taste.

Guaiacol Carbonate.—A white, odorless, tasteless powder, insol. in water, very sol. in chloroform, less sol. in alcohol, and in ether. It fuses at 87° C.

It is decomposed when treated with an alcoholic, KOH sol., and from the sol. so obtained guaiacol may be separated on the addition of an acid, and identified by appropriate test.

Betanaphthol, *Naphthol U. S. P.* 1890—A crystalline or pale buff-colored or colorless powder, having a faint phenol-like odor. Very sparingly sol. in water, very sol. in volatile solvents and in alkali-hydroxid solutions. A cold sat. sol. mixed with NH_4OH = a faint bluish fluorescence.

A sol. of betanaphthol in KOH sol. (1:4) treated with a little chloroform and heated gives a blue color changing to green and then to brown. An aqueous sol. treated with Fe_2Cl_6 gives a greenish color, and after some time white flakes separate which turn brown when heated.

Salol, *Phenyl Salicylate.*—A white, crystalline powder, having a faint aromatic odor. Insol. in water, very sol. in the volatile solvents.

With Fe_2Cl_6 a violet color is produced.

If a few grams of salol be dissolved in warm NaOH sol. and the resulting sol. acidified with HCl, a ppt. of salicylic acid forms, and the odor of phenol is recognizable.

Guaiacol.—A colorless crystalline solid or a colorless refractive liquid having an agreeable aromatic odor. Sol. in 53 parts of water, and in alcohol and ether in all proportions, and in acetic acid.

The addition of Fe_2Cl_6 to an alcoholic sol. of guaiacol (1:100) = an immediate blue color changing to green and then to brown.

Terpin Hydrate.—(*a*) It melts when quickly heated, and sublimes in fine needles. When strongly heated on platinum it burns with a bright smoky flame leaving no residue.

(*b*) If to its hot aqueous sol. a few drops of H_2SO_4 be added, the liquid will become turbid and develop a strongly aromatic odor.

Step VII.—If the substance is a liquid, possessing a characteristic odor, limpidity or viscosity, place about 1 cc. in a test-tube and apply *gentle* heat (water-bath). If it is completely volatilized, look for it under A. If it is not completely volatilized by gentle heat look for it under B.

Step VIII.—If the substance comes into Class A, place 1 cc. of it into a test-tube and add 10 cc. of water, and note if it is miscible or not.

(*a*) If it is miscible, it may be *Acetaldehyd, Acetic Ether, Ether, Paraldehyd, Formaldehyd, Ethyl Alcohol, Methyl Alcohol.*

(*b*) If it is not miscible or soluble in 10 parts of water or more, it may be *Chloroform, Benzin, Benzene, Cinnaldehyd, Amyl Alcohol, Amyl Nitrite, Benzaldehyd.*

CLASS A. DIVISION *a*. LIQUIDS MISCIBLE WITH WATER.

Ethyl Alcohol, *Grain Alcohol.*—A colorless, mobile, volatile and inflammable liquid. Miscible with water in all proportions.

The Oxidation Test. To the alcohol add some $K_2Cr_2O_7$ and a small quantity of H_2SO_4, and heat = a greenish color and an odor of aldehyd.

$$6C_2H_5OH + K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + \underbrace{6C_2H_3OH}_{\text{Aldehyde.}} + 7H_2O.$$

The Acetic Ether Test. To a small portion of the alcohol add some $KC_2H_3O_2$ and a little H_2SO_4 and warm the mixture = an odor of apples due to formation of acetic ether.

$$KC_2H_3O_2 + C_2H_5OH + H_2SO_4 = KHSO_4 + \underbrace{C_2H_5C_2H_3O_2}_{\text{Acetic Ether.}} + H_2O$$

The Iodoform Test (Leiben). Warm a small quantity of the alcohol with KOH and add some solution of iodin = a yellow ppt. of iodoform, forming slowly. Detects 12:000.

$$C_2H_5OH + I_8 + 6KOH = \underbrace{CHI_3}_{\text{Iodoform.}} + \underbrace{KCOOH}_{\text{Potass formate.}} + 5KI + 5H_2O$$

The Molybdic Test. A 10% sol. of molybdic acid in strong H_2SO_4 warmed with the alcoholic liquid = a blue color. Detects 1:1000.

Methyl Alcohol, *Carbinol, Wood Alcohol.*—A colorless volatile, inflammable liquid having a characteristic odor, and miscible with water in all proportions. It forms with dry $CaCl_2$ a crystalline compound.

The Salicylate Test. To a concentrated solution of sodium salicylate add some methyl alcohol and a few drops of H_2SO_4, and warm the mixture = an odor of oil of winter-green (methyl salicylate) develops:

$$HC_7H_5O_3 + CH_3OH = \underbrace{CH_3C_7H_5O_3}_{\text{Methyl Salicylate.}} + H_2O.$$

Methods for the Detection of Methyl Alcohol in Grain Alcohol, Pharmaceutical Preparations, Beverages, etc.

The Resorcinol Test. A spiral of copper wire is heated to redness and plunged into the liquid. One drop of a 0.5% aqueous resorcinol solution is added and the mixture floated on conc. H_2SO_4. A rose-red zone at line of contact = methyl alcohol; above the zone a scanty white or pinkish-white coagulum appears which finally separates and rises in purplish flakes.

Similar reactions are given with tertiary-butyl alcohols, dimethylethylcarbinol and formic acid, but the succession of colors and the deportment of the flaky coloring matter are different. If the methyl-alcohol solution is very dilute, repeat the immersion of the copper-wire coil several times. If the solution is concentrated, it should be diluted so as to be about 10% by volume. (Mulliken and Scudder, Am. Ch. J., Vol. XXI., 226.)

The Phloroglucin Test. The oxidation of methyl alcohol is the same as in the foregoing; acetaldehyd is removed by adding to the liquid remaining in the test-tube 6 cc. of a 3% H_2O_2 sol. and filtering into a porcelain dish. After 3 minutes add 2 cc. 10% sol. of $Na_2S_2O_3$, and then 3 cc. of a phloroglucin sol. made by dissolving 1 grm. of phloroglucin and 20 grm. of NaOH in water to make 100 cc. = a bright red color develops if methyl alcohol is present, the intensity of the color being in some degree proportionate

to the quantity of methyl alcohol present. Authority same as preceding test.

Prescott's Modification of the Foregoing Tests (see A. J. of Ph., Vol. 77, 108, Sadtler). The spirit tested should be diluted to about 10%. The copper wire is plunged into the liquid, held there for a second or two, then withdrawn and dipped into water to cool. This is repeated 5 or 6 times, the test-tube being immersed in cold water to keep contents cool. The liquid is then filtered into a wide test-tube and gently boiled to drive off acetaldehyd. The boiling should be continued until no odor of acetaldehyd is perceptible. Then the liquid is poured into a white porcelain dish and 1 cc. of the phloroglucin-alkali solution described in previous test added. A deep-red persisting color = methyl alcohol (formaldehyd reaction); a pale or slightly yellowish-red fading rapidly is due to acetaldehyd and indicates only ethyl alcohol.

The Rimini Test, Modified (Haigh, Ph. Rev., Oct., 1903). The oxidation of the methyl alcohol and the removal of acetaldehyd by boiling is effected as in foregoing tests. Then 1 cc. of a dilute sol. of phenylhydrazine hydrochlorid is added, followed by a few drops of a fresh sol. of sodium nitroprusside and finally by 1 cc. of 50% sol. of NaOH; if formaldehyd is present a light-blue or green color results, depending upon the amount of CH_3OH present. If the latter is absent, the color is greenish yellow. The method in which resorcinol is used seems to be the most satisfactory, and the new U. S. P. method is based upon its use.

The Resorcinol Test of the U. S. P., 8th Dec. Revis., is in substance as follows: 1 cc. of the spirit is diluted with water to make 10 cc. If the alcohol is already diluted, a correspondingly larger volume of it should be taken and diluted to 10 cc., so that the proportion of alcohol in the liquid shall not be more than about 10% by volume. A copper-wire spiral (of stated dimensions) should be heated to

redness in a flame free from soot, and plunged quite to the bottom of the spirit in a test-tube and held there for a second or two, then withdrawn and dipped into water to cool. This is repeated 5 or 6 times, immersing the tube in cold water to keep down the temperature of the liquid; it is now filtered into a wide test-tube and gently boiled, until the odor of acetaldehyd is no longer clearly distinguished. The liquid is now cooled, and to it added 1 drop of $\frac{1}{2}\%$ aqueous solution of resorcinol. A portion of this liquid is then floated upon conc. H_2SO_4 in another test-tube, being careful that the liquids do not mix. This tube, after standing 3 minutes, is slowly rotated, and at the line of contact a bright rose-red ring will appear and indicate methyl alcohol.

Miller's Test. (Oxidation with Dichromate) P. J. Tr., 2d Ser. VII, 318. Take $\frac{1}{2}$ ounce of the spirit, distil off about 1 dram. Then place in a small distilling-flask 30 grains of $K_2Cr_2O_7$, 4 fl. drams of water, and 30 minims of conc. H_2SO_4. To this add 30 to 40 minims of the above distillate and let stand 15 minutes. Then distil off about $\frac{1}{2}$ of the quantity, and to the distillate add Na_2CO_3 in slight excess, and boil down to 2 fl. drams. Then acidulate feebly with $HC_2H_3O_2$ and add 1 grain of $AgNO_3$ in 30 minims of water and heat gently. If the liquid merely darkens, but remains translucent, CH_3OH is absent, but if a copious ppt. of metallic silver falls and a thin film of silver lines the tube, methyl alcohol (CH_3OH) is present.

NOTE.—This test depends upon oxidizing CH_3OH to formic acid (HCOOH), which reduces silver.

$$CH_3OH + O_2 = HCOOH + H_2O.$$

The ethyl alcohol present is oxidized to acetic acid, which does not reduce silver. Aldehyd, which is produced at the same time and which does reduce silver, is removed by boiling with Na_2CO_3.

Sieker's Method (Am. Dr., Mch. 25, '01, and Ph. Rev., '01, 117). This method is based upon the oxidation to formaldehyd by a heated copper-wire spiral, and has the advantage of rapidity. Pour 4 to 8 cc. of the spirit into a test-tube and warm gently; immediately insert into the tube (not into the liquid) a copper-wire spiral which has been previously heated to dull redness; withdraw and reinsert the spiral several times, and it will be observed that a strong odor of *formaldehyd* is evolved, while the spiral will change in color from black CuO to red Cu upon inserting it, and will resume its black color each time it is withdrawn into the air.

NOTE.—Heating the copper wire oxidizes it to CuO. The warm methyl-alcohol vapor reduces the CuO to Cu and is itself oxidized to formaldehyd.

$$CH_3OH + CuO = HCOH + H_2O + Cu.$$

Ethyl alcohol reduces CuO in the same manner, but the odor of formaldehyd and of formic acid distinguishes the methyl alcohol.

Acetaldehyd.—Colorless, limpid, inflammable, possessing a fruity odor. Boiling-point 20.8° C. Miscible with water, alcohol, ether, and benzin.

(1) With solution of Ag_2O in ammonia, gives a bright mirror of silver on warming. KOH facilitates the reaction.

(2) It reduces Fehling's solution on being boiled, depositing a red ppt. of Cu_2O, and being thus converted into acetic acid:

$$C_2H_4O + O = HC_2H_3O_2.$$

(3) Heated with KOH it acquires a brown color.

(4) Rosaniline solution bleached by SO_2, gives a pinkish-violet color with aldehyd.

Paraldehyd.—A limpid liquid, colorless, possessing an odor resembling that of aldehyd. Soluble in 8 parts of water. Boils at 124° C., evolving inflammable vapors. Distilled with dilute H_2SO_4 it is again converted into aldehyd, of which paraldehyd is a polymer; its formula is $C_6H_{12}O_3$ (which is the formula of aldehyd (C_2H_4O) taken three times).

(1) Boiled with KOH it gives no brown color (distinction from aldehyd).

(2) Heated with Ammonio-Argentic-Nitrate, it produces a mirror of metallic silver.

Formaldehyd, *Formalin, Formic Aldehyd* (CHOH).—Miscible with water and alcohol, possessing a pungent odor of hamamelis extract; highly antiseptic liquid.

(1) With Sulfo-ferric-chlorid Reagent (Lyons) (Tinct. Fe_2Cl_6, U.S.P. 1 p. strong H_2SO_4, 25 p.). Underlay 2 cc. of the solution to be tested (distillate if necessary) with 2 cc. of the Sulfo-ferric-chlorid solution as carefully as possible = a pink to violet-blue zone will be formed; reaction very delicate.

(2) With the Morphine-sulfuric Reagent (Morphine 0.12 gm. in strong C. P., H_2SO_4 3 cc.). Underlay the distillate or a solution of CHOH with 2 cc. of the reagent; a purple-red color changing to violet will form. (By mixing 3 drops of 40% Formaldehyd with 3 cc. of pure strong H_2SO_4, a reagent is obtained which gives a similar reaction with Morphine (very reliable).

Heated with ammonio-argentic-nitrate solution = a gray ppt. of metallic silver and a deposit of silver in form of mirror on sides of tube.

To a little H_2SO_4 in which some salicylic acid has been dissolved, the addition of two drops of formaldehyd solution will produce a permanent deep red color on warming.

Ether, *Ethyl Oxid.*—A colorless, mobile, highly inflammable liquid of characteristic odor, boiling at 35.5° C., miscible

with 10 times its volume of water, and very readily miscible with alcohol, chloroform, benzin, benzene, and oils. It dissolves fats and resins.

Acetic Ether, *Ethyl Acetate.*—A colorless, limpid, inflammable liquid, possessing a fragrant acetous odor resembling that of apples. It boils at 72° C., and is miscible in all proportions with alcohol and with 7 parts of water.

Boiled with KOH sol. the residue gives reactions of acetates. Distilled with KOH sol. alcohol is produced, and distils over, and the distillate gives the reactions for ethyl alcohol:

$$C_2H_5C_2H_3O_2 + KOH = KC_2H_3O_2 + C_2H_5OH.$$

Class A. Division *b*. Liquids not Miscible with Water.

Chloroform, *Trichlor Methane,* $CHCl_3$.—A heavy, clear, colorless, mobile liquid of a characteristic odor. It is very volatile, not inflammable, and not miscible with water.

(1) To a small quantity of chloroform in a test-tube add some alcoholic sol. of NaOH, and a drop or two of aniline, and warm gently. There will be developed a very offensive odor of phenylisocyanid.

(2) Boil a few drops of chloroform with KOH sol. and add a fragment of resorcinol. An intense red color appears (rosolic acid).

(3) A few drops of chloroform, heated with a sol. of betanaphthol in strong KOH sol. develops a fine blue color, changing to green and brown.

Benzin, *Petroleum Ether.*—A clear, colorless liquid, of a strong characteristic odor, resembling that of kerosene. It is very inflammable, and is not miscible with water. It boils at 45° to 60° C.

Benzene = *Benzol* = *Coal-tar Benzene.*—A limpid liquid possessing an aromatic benzin-like odor. Should not be confounded with petroleum benzin.

Boiling-point 80° C. Miscible with alcohol, ether and chloroform, insoluble in water. Chemical formula C_6H_6.

(1) Mixed with strong HNO_3 (avoiding overheating) nitrobenzene (oil of mirbane), $C_6H_5NO_2$, is formed, which, poured into cold water, separates in oily drops possessing the characteristic odor of essential oil of bitter almonds.

(2) Mixed with strong H_2SO_4 and boiled with KOH, a phenolsulfonate is obtained which should be tested for.

Amylic Alcohol (*Fusel Oil*). A limpid oily liquid possessing the odor of whiskey; miscible with alcohol, but very sparingly with water. Boils at 127° C.

(1) Warmed with dilute H_2SO_4 and $NaC_2H_3O_2$, it forms amyl acetate ($C_5H_{11}C_2H_3O_2$) possessing the odor of pears, and known as "pear oil."

(2) Distilled with H_2SO_4 and $K_2Cr_2O_7$ and the distillate boiled with KOH, it forms potassium valerate. Apply the tests for valerates.

Amyl Nitrite, $C_5H_{11}NO_2$.—A clear yellowish liquid of an ethereal banana-like odor.

Insol. in water. Freely miscible with alcohol or ether, very volatile even at low temperature and very inflammable, burning with a smoky flame.

When mixed with potassium iodid and a drop or two of sulfuric acid, iodin is liberated, and colors starch blue.

Benzaldehyd, *Benzoic Aldehyd.*—A colorless, strongly refractive liquid having an odor like that of essential oil of bitter almonds. Insol. in water. It is converted into benzoic acid by oxidation.

Class B.

Phenol, *Carbolic Acid—Phenic Acid.*—The liquefied carbolic acid is a colorless liquid having a peculiar characteristic aromatic odor, miscible with water, and readily sol. in

alcohol, ether, chloroform and the alkalies. It cauterizes and whitens the skin when concentrated.

Creosote, an almost colorless or yellowish (pinkish or brown if impure), highly refractive, oily liquid having a penetrating, smoky odor; sol. in $HC_2H_3O_2$.

PHENOL.	CREOSOTE.
The Bromin Test.—Its aqueous sol. yields with bromin-water a white ppt. of tribromphenol, which at first redissolves, but on adding more of the reagent becomes permanent.	*The Bromin Test.*—Its aqueous sol. yields with bromin-water a reddish-brown ppt.
The Ferric-Chlorid Test.—10 cc. of aqueous sol. of phenol (1:100)+1 drop of Fe_2Cl_6 sol. The sol. becomes violet-blue, and the color is permanent.	*The Ferric-Chlorid Test.*—The liquid develops a violet tint, which is transient, changing rapidly to greenish and brown, and forming a brown ppt.
The Collodion Test—Equal volumes of phenol and collodion, stirred together in a dry test-tube, will form a permanent coagulum. This also occurs with albumen.	*The Collodion Test.*—No permanent coagulum results.
The Glycerin Test.—1 volume of cold liquefied phenol forms with 1 vol. of glycerin a clear liquid, which is not rendered turbid on the addition of 3 vols. of water.	*The Glycerin Test.*—1 vol. of creosote forms with 1 vol. of glycerin a clear liquid, from which $\frac{1}{4}$ vol. of water will cause separation of a creosotic layer equal to more than 1 vol. and render liquid turbid.
The KOH Test.—Not so with phenol.	*The KOH Test.*—1 cc. of creosote mixed with 10 cc. of KOH in absolute alcohol (1:5)=a solid crystalline mass.
Solidification Test.—Phenol sol. solidifies when cooled.	*Solidification Test.*—Creosote cooled to $-4°$ F. does not solidify, but it gelatinizes.
4 parts of phenol sol. mixed with 1 part of NH_4OH and a few drops of NaClO added and gently warmed =a blue to green color.	
Add H_2SO_4 to some benzaldehyd until the latter darkens, then add some phenol, and a red color is produced; now add some KOH=a violet.	

Glycerin. *Glycerol Propenylalcohol.*—A clear, colorless, thick, syrupy liquid, smooth to the touch, sweet to the taste, odorless, producing a sensation of warmth in the mouth. It absorbs moisture; sol. in all proportions in water and

alcohol, but not sol. in ether, chloroform, carbon disulfid, benzin or oils.

(1) *The Borax-Bead Test.* Add a few drops of glycerin to a little powdered borax; mix and dip the looped end of a platinum wire into the mixture, and hold in a Bunsen flame = a transient green color.

(2) *The Acrolein Test.* Heated alone or with H_2SO_4 to a high temperature an irritating odor of acrolein is produced.

(3) *The Borax Test.* A piece of blue litmus paper is shaken in a test-tube with a solution of borax, and a few drops of glycerin added. The litmus paper immediately becomes red. This is due to the liberation of boric acid by the glycerin. The addition of a little bicarbonate of soda to this mixture will cause effervescence.

(4) *The Permanganate Oxidation Tests.* Glycerin in a strongly alkaline sol. is oxidized by $KMnO_4$ and converted into oxalic acid.

Take 1 cc. of a weak sol. of glycerin, make it strongly alkaline with KOH, and add an excess of a saturated sol. of $KMnO_4$, i.e. until the mixture is blackish. Boil and add some Na_2SO_3 to destroy excess of $KMnO_4$, then filter, acidulate with $HC_2H_3O_2$, and add $CaCl_2$ = a white ppt. of CaC_2O_4 forms.

$$C_3H_5(OH)_3 + 4KMnO_4 = \underbrace{K_2C_2O_4}_{\text{Potassium Oxalate.}} + K_2CO_3 + 4MnO_2 + 4H_2O$$

$$K_2C_2O_4 + CaCl_2 = \underbrace{CaC_2O_4}_{\text{Calcium Oxalate.}} + 2KCl$$

NOTE. If the foregoing tests are to be applied to any mixture containing organic matters, a portion of the latter is evaporated to dryness at a temperature below 100° C. and the glycerin extracted from the residue by means of ether. The ethereal solution is then evaporated and the tests applied to the residue.

Nitrobenzene = *Nitrobenzol* (*Oil Mirbane*). A limpid, yellowish, oily liquid, possessing the odor of essential oil of bitter almonds.

(1) Placed in contact with zinc dust and dilute H_2SO_4, it is decomposed into aniline and water:

$$C_6H_5NO_2 + 3H_2 = C_6H_5NH_2 + 2H_2O.$$

(2) Heat the aniline solution as obtained above with a few drops of $CHCl_3$ and KOH. The characteristic odor of phenylisocyanid will be recognized.

(3) Drop a small crystal of $KClO_3$ into some nitrobenzene, and underlay this with H_2SO_4; a violet color will develop.

90. SCHEME FOR THE IDENTIFICATION OF ACETANILIDE, PHENACETIN, QUININE SULFATE.—F. S. HYDE.*

Pure substance.	Melting-point. C.	Solubility in water.	Solution of substance in water. Boiled with excess of KOH and a few drops of chloroform	Solution of substance in water. Ferric chlorid.	Solution of substance in water. Dilute nitric acid.	Solution of substance in water. Bromin-water.
Acetanilide (Phenylacetamide) $C_6H_5NH.COCH_3$.	113°	Soluble in cold; more so in hot.	Odor of isonitrile.	Yellow solution. Red on boiling.	Colorless.	White crystals. Para-bromo-acetanilide.
Exalgine (Methyl Phenylacetamide) $C_6H_5N.CH_3.COCH_3$.	101°	Not very soluble, cold; easily soluble, hot.	No odor of isonitrile. Class of secondary amines.	Yellow solution. Cloudy red on boiling.	Colorless.	No precipitate.
Phenacetin (Acetylparaamidophenetol) $C_1H_4.OC_2H_5.NH.CO$.	135°	Soluble with difficulty.	Odor of isonitrile.	Yellow solution. Blood-red on boiling.	Cloudy yellow solution. Crystals ofnitro compound.	No precipitate.
Phenecoll hydrochloride (Glycocollparaamidophenetol) $C_6H_4<{OC_2H_5. \atop NH.COCH_2.NH_2.HCl.}$	No. M.P. HCl Comp.	Very soluble.	Odor of isonitrile.	Yellow solution. Darkens and orange precipitate on boiling.	Colorless.	No preeipitate.
Salol (Phenyl salicylate) $C_6H_4.OH.COO.C_6H_5$.	43°	Soluble with difficulty.	No odor of isonitrile. Yellow solution.	Yellow solution. Blood-red on boiling.	Colorless.	No precipitate cold; white cloudy compound on boiling.
Resorcinol (Metadioxybenzene) $C_6H_4(OH)_2$.	118°	Easily soluble.	No odor of isonitrile. Carmine-red solution.	Dark violet. Yellowish on adding drop of sulfuric acid.	Yellow solution.	Yellowish precipitate dissolving immediately.
Quinine sulfate $C_{20}H_{24}N_2O_2.H_2SO_4$.	....	Slightly soluble. With few drops of sulfuric acid dissolves with blue fluorescence.	Base precipitates and dissolves on heating.	Yellow solution	Colorless with bluish fluorescence.	Dry substance on porcelain with weak bromin-water gives green coloration on adding two or three drops ammonia-water = Thallieo quin test.
Antipyrine (Phenyldimethylpyrazolon) $HOC_3N_2(CH_3)_2C_6H_5$.	113°	Soluble.	Nothing.	Blood-red. Disappears on adding a drop of sulfuric acid.	Colorless.	Yellowish-white precipitate.

* J. Am. Chem. Soc., Vol. XVII, page 933.

91. PROFESSOR E. H. BARTLEY'S* SCHEME FOR THE IDENTIFICATION OF ORGANIC SUBSTANCES COMMONLY USED IN PHARMACY, MEDICINE, AND THE ARTS.

Inspection.

Observe the *color, consistency,* if a liquid, *odor, taste,* etc.

1. The **Color** of definite chemical compounds of organic origin is characteristic only when they are in a pure state. When impure, the color is of little service.

Note. The first thing to determine in any given substance is whether it is a definite compound or a mixture. If a liquid, this is best determined by distillation when this is possible, having care at the same time to determine its boiling-point, or if more than one liquid can be distilled off, the boiling-point of each, and collecting each by itself. If the substance be a solid, it is best to examine it under a microscope of low power to determine whether it be homogeneous, crystalline, amorphous, or a mixture. If a mixture, it may often happen that the substances may be separated by a proper choice of solvents, observing the effects under the lens. Crude powdered drugs and bodies like starch, pollen, talcum, etc., may be readily identified in this way.

2. The **Consistency** of a liquid, whether viscid, oily, mobile, volatile, fixed, etc., both cold and warm, is of much importance, and often gives a clue to its identity.

3. The **Odor** of some organic compounds, especially the liquids and some of the solids, is so characteristic as to be of great service in giving a clue to their identity, or to the exclusion of certain substances. When the substance has a distinct odor it is of great service. Some liquids give off their characteristic odor better while warm than when cold When the

* From hectographed sheets as used by the post-graduate class in the Brooklyn College of Pharmacy.

odor is identified, it is best to compare that of the substance under examination with that of a known substance which it is known to resemble.

Odors are described as *ethereal, alcoholic, pungent, ammoniacal, terebenthinate, camphoraceous, aromatic, tarry, putrid, sulphurous,* etc.

4. The **Taste** of some organic compounds is highly characteristic, especially in dilute solutions.

Tastes are described as:

Sweet, as that of the higher alcohols, glycerin, mannit, etc., the sugars and saccharin.

Sour, as that of the soluble acids and acid salts.

Bitter, as that of the alkaloids, glucosides, tannic, gallic, and picric acids, and some resinous and bitter principles of plants.

Aromatic, as that of certain essential oils or their derivatives, the aromatic hydrocarbons or their derivatives, the phenols, cresols, aniline, and their derivatives.

Burning, as that of alcohol, chloroform, carbolic, etc. The burning taste is usually only obtained with the pure substance.

Camphoraceous, terebenthinate, tarry, empyreumatic, and similar terms are descriptive by comparison with well-known substances.

CAUTION! *Never taste a pure substance of which you know nothing.* Make a dilute solution in alcohol or water (about 1%) and then taste cautiously.

SEPARATION OF ORGANIC COMPOUNDS INTO GROUPS.

A. *Heat a small fragment of the dry substance on a piece of platinum foil or fine iron-wire gauze.*

1. It *evaporates,* but neither chars nor ignites: it is *water.* If a residue is left, note its behavior on heating.
2. It *chars* or ignites and burns = **an organic body.** Leaves a residue = organic salt of a metal.

Residue alkaline to litmus and effervesces with HCl = alkaline metal. (See flame reactions under B.)

It chars and gives odor of burning hair or a pungent tarry odor = nitrogenous matter or an alkaloid.

3. It does not char and does not burn away *inorganic.*
4. It chars and gives odor of SO_2 = organic compounds rich in sulfur. (See N.)

If the substance is a liquid, note whether it gives off soot when burning. Remove from flame after ignition takes place and observe odor of the smoke.

NOTES: Almost all hydrocarbons, aromatic compounds, and complex organic compounds containing more than 4 carbon atoms give off soot in burning.

The lower alcohols containing less than 5 carbon atoms, the simpler ethers, aldehyds, ketones, and other derivatives of the methane series having less than 4 carbon atoms usually give off no soot in burning.

B. *Heat a fragment of the substance, or a drop of the liquid, in the loop of a clean platinum wire.*

1. The flame is tinged with green: Halogen in absence of Ba or boric acid. If green is obtained use copper wire previously heated in outer edge of Bunsen flame, when the green color is much brighter if halogens be present.
2. The flame is violet: Salts of potassium. View through cobalt glass. Substance leaves residue, test as in A.
3. The flame is yellow: Sodium.
4. The flame is red: Lithium or strontium.

C. *The Detection and Removal of Water.*—If the substance is a solid it should be dried well before treatment as described below in E.

Liquids: (1) To 5 cc. of the liquid add 0.5 to 1 grm. of fused and pulverized K_2CO_3, shake well, and let stand for a half-hour. If water be present the K_2CO_3 will entirely dissolve, or will dissolve in the water present and separate as a layer at the bottom.

Or, (2) To 5 cc. of the liquid add 1 grm. of recently ignited (dehydrated) copper sulfate. The presence of water is shown by the $CuSO_4$ assuming a blue color within a half-hour.

Effervescence (1) indicates the presence of an acid or acid salt. A white precipitate is most likely, *though not always,* due to the precipitation of an alkaloid.

D. *If water be present,* boil a portion of the liquid in a test-tube and test the inflammability of the vapor in the mouth of the tube, to prove the presence or absence of a volatile organic liquid. *If no inflammable vapors are obtained,* evaporate a few cc. in a watch-glass on a water-bath to dryness or to a syrupy consistency. The residue, if any, or the concentrated liquid free from water, may be tested as below described.

If inflammable vapors are obtained, distil off a portion of the volatile liquid and apply the tests to the distillate.

The liquid to which the following tests are applied must first be freed from water, by agitation with fused K_2CO_3 or $CaCl_2$, and allowed to stand a half-hour.

Ultimate Qualitative Analysis of Organic Compounds.

All non-gaseous bodies combustible in the air are organic and hence contain *carbon* and *hydrogen.*

E. *To Detect other Elements.*—Put in a clean dry matrass of hard glass about 0.1 grm. of clean sodium and heat carefully over a flame until a part of the metal is converted into vapor, and let fall two or three drops of the liquid, or a corresponding amount of the solid, directly upon the fused metal. Allow the mixture and tube to cool, add a few drops (1 cc.) of alcohol to dissolve unchanged sodium, then a few cc. of distilled water, and filter through a small filter. Test the solution as follows:

For *sulfids,* with a copper coin, or by a drop on filter-paper wet with lead acetate solution.

For *sulfur and nitrogen together*, by acidifying with HCl and adding Fe_2Cl_6, when the red color of ferric sulfocyanid will appear.

For *nitrogen without sulfur*, by testing for cyanids by adding NaOH and a mixture of ferrous and ferric salts, and then acidifying with HCl = blue color.

For *chlorin*, with HNO_3 and $AgNO_3$, when S is present, boiling with excess of NHO_3 before adding the $AgNO_3$; soluble in NH_4OH.

For *bromin* and *iodin*, by acidifying with HCl, adding chlorin water, and then chloroform or starch solution.

For *halogens* (confirmatory), heat a loop of copper wire in the outer flame of Bunsen burner, cool, dip in substance, and heat again = green flame, *halogen*.

For *nitrogen* (confirmatory), heat the substance with soda-lime—most nitrogenous compounds, except nitro compounds, give off ammonia—and test vapors with moist reddened litmus paper in mouth of tube or glass rod wet with HCl.

Nitrogenous animal matter usually gives off the odor of burnt horn or hair on being heated dry; *alkaloids* and *amin derivatives* give a pungent tarry odor.

Having determined what elements are present, we next determine the *class* or *group* to which they belong.

F. *Acids and Bases.*—Test reactions with red and blue litmus for *free acids, acid salts*, and *bases*. Solids must be brought into solution in water or alcohol. Most acids are soluble enough to react acid with litmus. Confirm by warming with K_2CO_3 or Na_2CO_3 = effervescence.

Organic bases are usually nitrogenous, and aliphatic amins, aromatic amins with the amid group in the side chain, free alkaloids or some of the artificial bases. In the last case they are black or dark liquids of a strong offensive odor. All these bodies except aliphatic amins are insoluble

in water, but dissolve as a rule in dilute acids to form crystallizable salts.

When heated with NaOH solution the *amids, imids,* and *nitrils* evolve NH_3.

Amins do not evolve NH_3 with NaOH solution; give pungent fumes at red heat.

Amins containing the lower alcohol radicals are soluble in water and dissolve in weak acids to form salts. These salts as well as the amins containing higher radicals are soluble in alcohol. This distinguishes them from ammonium salts.

G. *The substance contains no nitrogen.*—To 2 cc. of the thoroughly dried liquid in a dry test-tube add a small fragment of metallic sodium. If no action ensues warm the solution. Viscid liquids and solids should be dissolved in anhydrous alcohol-free ether or in petroleum ether before adding the sodium.

Bodies containing hydroxyl slowly evolve hydrogen with metallic sodium.

Besides hydroxyl compounds, some *aldehydes, ketones, esters,* and *amids* evolve hydrogen. The halogen compounds of methyl and ethyl evolve gaseous hydrocarbons. A few hydroxyl compounds, as resorcinol and salicylic acid, do not give off hydrogen with sodium.

Rapid evolution of hydrogen will suggest water as an impurity.

The acids will have been identified under F. *Amids* will have been detected under F, and will contain nitrogen, which excludes them from this group of compounds. The *halogen compounds* will have been detected by flame reaction under E.

The odor of the original substance will be of assistance here.

The aromatic compounds (phenols, cresols, tannins, etc.) and hydrocarbons will have been suspected from giving

soot in burning under A, and from odor and oily appearance if liquid.

No hydrogen is given off by hydrocarbons.—No action, even on warming, will then generally indicate that the substance is not an alcohol, a phenol, or an acid.

H. Treat a portion of the original solution, or liquid, with a few drops of Fe_2Cl_6; *the solution must be neutral.* Phenol, resorcinol, and salicylic acid give violet, orcin blue-violet, pyrocatechin a green, and pyrogallol red and a blue with $FeSO_4$ and $Fe_2(SO_4)_3$.

Naphthol, the nitrophenols and para oxacids do not give a color with Fe_2Cl_6.

I. Treat a small portion of the substance on a watch-glass with strong H_2SO_4; or, if a liquid, add 2 cc. of C.P. H_2SO_4 to 1 cc. of liquid, keep cool by immersion in water, and shake well, and observe any action or change in color.

Solids may not be acted on, may be dissolved without change, may be dissolved with change of color, or may be dehydrated and charred.

Liquids may not be acted upon (as monatomic, primary alcohols and saturated hydrocarbons), may be dissolved without change, may combine with the acid with evolution of heat, or may be decomposed with blackening, etc. Cold H_2SO_4 does not affect saturated or aromatic hydrocarbons or their haloid derivatives; most other compounds are either dissolved or decomposed.

After observing the action in the cold, warm and note any change.

Hot H_2SO_4 esterifies monatomic primary alcohols, and unites with unsaturated hydrocarbons of aliphatic series and aromatic hydrocarbons and most of their derivatives.

Pour the mixture into twice its volume of water and measure the volume of any separated liquid to see if it has suffered any loss in volume.

Separate the undissolved portion, if a liquid, and reserve for further tests.

J. To another portion of the liquid known to contain no nitrogen, or to the solid brought into solution in chloroform or carbon tetrachlorid, add, drop by drop, a distinct excess of bromin in solution in water, or in chloroform or CCl_4.

1. A *precipitate* (tribromphenol) indicates a phenol (but few exceptions). Many aromatic amins also give this reaction (see Fe_2Cl_6 reaction under H).
2. *An instantaneous decolorization* without subsequent precipitate and without evolution of HBr indicates addition, and probably unsaturated hydrocarbons.
3. *Decolorization with evolution of HBr* shows *substitution* and may occur with an aldehyde, a ketone, a phenol, or an amin. In last case without evolution of HBr.
4. *Production of heat in oils.*
5. *No decolorization* with saturated hydrocarbons, alcohols, or esters of fatty series.

K. *Test the solubility of the substance in water and then treat it with cold 10% solution of KOH* and observe the result.

1. *The substance dissolves in KOH solution, and also in pure water;* no deduction can be drawn.
2. *The substance is insoluble in water and soluble in 10% KOH = many esters*, with separation of the alcohol, which may be detected by odor or by appropriate tests applied to distillate.

   Esters of higher alcohol radicals are not *usually* saponified by cold dilute KOH, but may be by heating the mixture. The alcohol will then usually separate as a distinct layer; the acid remains in solution as a salt of potassium = *many organic acids and phenols* (see F and H).

   All free organic acids dissolve in cold KOH solution.

   After separating any alcohol or undissolved liquid or solid, acidify a portion of the KOH solution with HCl.

Observe if any acid separates, or if on warming any acid odor develops; apply the regular tests for acids.

3. Neutralize a portion of the KOH solution and apply the usual tests for the acids.
4. Insoluble in water and insoluble in cold 10% KOH solution: Hydrocarbons, higher alcohols, ethers, some phenols, and phenol derivatives.

L. If the substance is not affected by cold 10% KOH solution, heat a portion of it to boiling for three to five minutes with a strong solution of KOH.

1. The substance is not affected: Hydrocarbons, most alcohols, ethers, etc.
2. The substance is dissolved and does not separate on cooling, or, if so, it has a different odor and behavior from original substances: Esters not saponified under K. 3, including the fixed oils, some phenols, cresols, and halogen compounds of hydrocarbon radicals.

   The halogens are not removed, as a rule, from the radical of substitution compounds.

   Aldehyds are generally decomposed by strong KOH, with formation of a hydrocarbon and potassium formate. The decomposition of aliphatic haloid compounds yields alcohols, and of aromatic halogen compounds they yield phenols or hydrocarbons.

   Dilute the solution formed by boiling with strong KOH, with 5 parts of cold water, and note whether there is a separation of a liquid, the formation of an emulsion, or a precipitate, and whether the liquid or solid thus separating resembles the original substance.

M. 1. Whether *solution* or *decomposition* takes place in K or L, separate the solution of KOH from any undissolved substance and faintly acidify with HCl, and test the solution for organic acids.

   If a separation of a liquid or solid takes place on acidifying, this is an organic acid, a phenol, a cresol or

a resin. Formic, hydrocyanic, acetic, propionic, citric, tartaric, succinic, butyric, oxalic, meconic, valeric, malic, tannic, gallic, and picric acids will remain in solution after acidifying. Oleic, stearic, palmitic, the resin acids and other higher fatty acids, the phenols, cresols, and aromatic acids will separate on acidifying.

2. Acidify another portion of the KOH solution with HNO_3 and test for halogens with $AgNO_3$ in the usual way.

The substance contains sulfur and no nitrogen.—The substance gives off SO_2 when heated on platinum foil, or gives the reaction for sulfur when heated with sodium: The substance is a sulfate, a sulfuric ester, a sulfite, a sulfurous ester, a sulfonic acid, a sulfone (sulfonal, trional, tetronal), a sulfid, a mercaptan, a thioaldehyd, a thioketone, or volatile oil of mustard.

The *sulfones* give off SO_2 when heated on platinum foil. When melted in a dry test-tube and then a little gallic or pyrogallic acid dropped in, it turns brown and gives off the odor of *mercaptan.*

Sulfuric esters and *sulfurous esters* are easily saponified when heated with strong HCl, the latter giving off SO_2. Barium chlorid gives a precipitate with the former after treating it with HCl. A *sulfite* gives off SO_2 with HCl, and a *sulfid* gives off H_2S.

Sulfonic acid and *sulfonates* only decompose when fused with KOH or NaOH. The solution of the fused mass, after acidification with HCl, gives $BaSO_4$ with $BaCl_2$.

Mercaptan will be recognized by its odor of garlic or asafœtida.

92. SUMMARY OF NON-NITROGENOUS CLASSES OF ORGANIC BODIES.

Organic Acids give acid reaction to litmus paper and are mostly soluble. Exceptions: Benzoic, salicylic, and fatty acids containing more than 4 carbon atoms (valeric 1 in 27 of water). Lower members have characteristic odors. Polybasic acids are usually soluble in water; higher fatty acids insoluble.

For sulfonic acids see above.

Free Nitrogen Bases react alkaline to litmus. Amins with lower fatty radicals, aromatic radicals, or alkaloids all combine with acids to form salts; they are usually soluble in water and all are soluble in alcohol. Alkaloids and amin bases when heated in the test-tube or crucible yield pungent, offensive vapors. The vapors of salts react acid with litmus paper held in mouth of tube. Morphine (alkaloid) gives an alkaline vapor.

Hydrocarbons burn with a smoky flame, giving soot; are all insoluble in water, contain no nitrogen, and do not evolve hydrogen with sodium.

Saturated hydrocarbons do not react with bromin or sulfuric acid, or KOH solutions.

Unsaturated hydrocarbons dissolve in cold C.P. H_2SO_4 as well as most other compounds, except saturated and aromatic hydrocarbons and their halogen derivatives, and usually instantly decolorize bromin solution, without evolving HBr.

Aromatic hydrocarbons form sulfonic acids with hot H_2SO_4 and dissolve.

Alcohols.—Monatomic alcohols having less than 4 carbon atoms are miscible with water, and burn without giving off soot. All alcohols give off hydrogen with metallic sodium, and esterize with strong H_2SO_4 and heat, and form esters with organic acids, when salts of these acids are warmed with the alcohol and H_2SO_4.

They are distinguished from phenols by reaction of latter with Fe_2Cl_6 and bromin water, *and from aldehyds* by their failure to restore the red color to a solution of fuchsin decolorized with H_2SO_3, or to form compounds with phenylhydrazin.

Behavior with bromin water distinguishes unsaturated alcohol radicals from saturated; from one another by boiling-point, etc.

Aldehyds. — Class identified by reaction with phenylhydrazin and colorless fuchsin; also by reaction with strong KOH solution and with bromin.

Evolve hydrogen with sodium. Not affected by H_2SO_4, except aldose group of carbohydrates. Form acids by oxidation with potassium permanganate, with separation of MnO_2.

Aldehyds reduce an ammoniacal solution of $AgNO_3$ on heating to boiling.

Ketones.—Acetone and most other ketones form precipitates with phenylhydrazin. Cold concentrated H_2SO_4 either dissolves or destroys aldehyds and ketones.

Sodium acid sulfite gives crystalline compound with acetone, and with all other ketones containing the group CH_3CO.

Acetone gives red color with a few drops of freshly made solution of sodium nitroprusside and ammonium hydroxid.

Acetone gives iodoform with iodin in KI and NH_4OH. Alcohols do not under these conditions, nor do aldehyds.

Ethers.—Ammonia, alkalies, cold dilute acids, sodium, and PCl_5 have no action on simple ethers.

Warmed with C.P. H_2SO_4 gives alcohol and alkyl sulfuric acid. The alcohol may be distilled off and tested. Neutralize the acid solution with $BaCO_3$, filter, and evaporate to dryness. $BaSO_4$ left; insoluble in HCl; or boil the filtrate from the $BaCO_3$ with C.P. HCl, when a precipitate of $BaSO_4$ will indicate the ethereal sulfuric acid and hence an ether.

Esters.—These are easily saponified by warming with 10% KOH solution. The alcohol distils off, and acid detected, after

neutralizing with HCl, by usual means. Boiling with strong HCl also decomposes them in some cases.

Halogen compounds of hydrocarbons of fatty series are decomposed by strong KOH solution. Boiling solution of alcoholic KOH sets free aromatic hydrocarbons from haloid compounds of these.

Strong KOH solution gives soap with fats and oils. Acidification sets free fatty acid. Bromin reacts with great energy upon fats and oils. Fats and oils are insoluble in water and soluble in ether.

Carbohydrates or **Saccharids** contain CH and O.

When heated on foil, they melt, char, swell up, and give off burnt-sugar odor, leaving voluminous charcoal (see A). They turn brown when heated with strong H_2SO_4 (see I).

They effervesce with metallic sodium (see G).

When their solutions are boiled with KOH solution they turn first yellow and then brown.

They are generally soluble in water (except cellulose, lignin, and tunicin), but are insoluble in strong alcohol. When heated in matrass or dry test-tube they decompose and give off water, which condenses in upper part of tube. Vapors acid.

Gums.—Soluble or partly soluble in water, and precipitated by alcohol. Watery solution viscid, and sticky on drying. Dextrin gives brown color with iodin; others give no color, except tragacanth, which often contains starch.

Organo-metallic Compounds.—These compounds leave a very considerable residue on heating the substance on platinum foil. They char or turn black on heating, and then gradually become lighter in color except when the metal is iron. They are chiefly compounds of iron, bismuth, mercury, aluminum, silver, cadmium (salicylate), cesium (tartrate), calcium, boron (boric acid), sodium, strontium, magnesium, lithium, potassium, magnesium, manganese, uranium (acetate), and zinc.

The metallic bases should first be determined by heating a portion of the substance until it chars, exhausting the charred

mass with nitric acid if lead, silver, or mercury be found, or with HCl when these metals are found to be absent by a preliminary trial with HNO_3.

The HCl solution is to be treated by the usual course of qualitative examination for the metals.

When the metal has been proven to be sodium or potassium or lithium, we may at once proceed with the examination for acid radicals in the aqueous solution of the substance.

When the metal is not one of the alkaline metals, treat the substance with dilute KOH solution and heat to boiling. Filter off any precipitate, render the solution acid with HCl.

If a precipitate forms on making the solution acid, filter. The acid so precipitated may be benzoic, salicylic, stearic, palmitic, oleic, phenol, cresol, or naphthol.

93. IDENTIFICATION OF SCALED IRON COMPOUNDS.*

JOSEPH L. MAYER.

STEP I.—Heat about 1 gram of the substance in a porcelain crucible to dull redness, allowing free access of air.

If an *odor* resembling that of *burning sugar* is given off, the substance is probably a *citrate* or *tartrate*. Confirm in Step IV.

When all the combustible matter is consumed, dissolve out the soluble part of the residue with a few cc. of hot water, and filter.

Test the filtrate with red litmus paper.

The paper turns *blue; sodium* or *potassium*, or both are present.

The paper remains *unchanged in color;* proceed to Step II.

Divide the solution which has turned red litmus blue into two parts.

(*a*) Heat on a clean platinum wire in a colorless flame: The flame becomes *intensely yellow; sodium* is present. Observe

* Drugg. Cir., Feb. 1901.

this flame through cobalt glass. If *violet-red, potassium* also is present.

The flame is colored *violet* only; *potassium* is present. Confirm under (*b*).

(*b*) Add to the solution some test solution of sodium-cobalt nitrite:

A *copious yellow precipitate* indicates *potassium.*

Step II.—Dissolve a small quantity of the original substance in water, acidulate with hydrochloric acid and divide into two parts. To one part add test solution of potassium ferrocyanid:

A *blue precipitate* indicates *ferric iron.*

To the other part add potassium ferrocyanid:

A *blue precipitate* indicates *ferrous iron.*

Step III.—Dissolve 2 grams of the original substance in 20 cc. of 10% solution of potassium hydroxid and boil; an *odor* of *ammonia* indicates the presence of *ammonium.*

Whether ammonium is present or not, cool the solution and filter; examine the filtrate as directed in Step IV, and the precipitate as in Step V.

Step IV.—The filtrate obtained in Step III should be clear and colorless and measure about 10 cc. Divide it into three portions of 2.5, 2.5 and 5 cc. respectively.

(*a*) Slightly acidulate one of the smaller portions with acetic acid and add test solution of calcium chlorid:

A *precipitate* occurs; the salt is probably a *pyrophosphate.* Confirm by (*c*).

Filter and boil the filtrate (or the clear solution if no precipitation has occurred):

A *white crystalline precipitate* occurring after a few minutes indicates a *citrate.*

(*b*) Slightly acidulate the second smaller portion with acetic acid and add an equal volume of alcohol:

A *white crystalline precipitate* occurring after a few minutes indicates a *tartrate.*

(*c*) To the remaining portion of (5 cc.) add 5 cc. of a 10% solution of ammonium chlorid, and then add, a few drops at a time, 1.5 cc. of a 10% solution of magnesium sulfate, agitating after each addition:

A *white crystalline precipitate* indicates a *phosphate.*

Confirm as follows: Thoroughly wash the precipitate until the wash-water gives no cloudiness with silver-nitrate solution, dissolve in dilute nitric acid, neutralize with ammonium hydroxid, acidify with acetic acid and add 5% solution of silver nitrate.

If a phosphate is present, a *canary-yellow precipitate* appears.

To the filtrate from the precipitate obtained by the addition of ammonium chlorid and magnesium sulfate to (*c*), or to the clear liquid if no precipitate was produced, add a little acetic acid and heat to boiling:

A *white flocculent precipitate* indicates a pyrophosphate.

Confirm by the silver-nitrate test applied as above:

A *white precipitate* appears if a *pyrophosphate* is present.

STEP V.—Wash the precipitate obtained in Step III. into a test-tube with about 15 cc. of chloroform, shake well for a few minutes, filter, and divide the filtrate into two portions (*a*) and (*b*). Heat both portions of the filtrate in porcelain capsules on a water-bath until the chloroform is all evaporated.

(*a*) Add a small quantity of hot water slightly acidulated with sulfuric acid to the residue in one of the capsules, and filter. Divide the filtrate into three equal parts.

1. Add to one portion Mayer's reagent:

A *precipitate* indicates an *alkaloid.*

2. Add to the second portion Labarraque's solution, using a quantity sufficient to destroy blue fluorescence if observed, and then a few drops of ammonium hydroxid:

An *emerald-green color* indicates *quinine.*

3. To the third portion add ammonium hydroxid in slight excess, filter, reject the filtrate, dissolve the precipitate in about 1 cc. of water, containing a few drops of diluted acetic

acid, neutralize exactly with potassium hydroxid, and add about 1 cc. of a saturated solution of Rochelle salt:

A *white precipitate* indicates *quinine* or *cinchonidine.*

Filter off the precipitate, dissolve in diluted hydrochloric acid, add potassium-hydroxid solution and 2 cc. of ether, and shake well. The quinine dissolves, while the cinchonidine remains as a crystalline precipitate at the line of separation of the two liquids.

To the filtrate from the precipitate in 3, or the clear solution if no precipitate was produced, add an excess of potassium hydroxid:

A *white precipitate insoluble in ether* indicates *cinchonine.*

(*b*) To the residue in the other capsule add a drop of sulfuric acid; into this put a fragment of potassium chromate, and after a few minutes draw this drop, by means of a glass rod, across the capsule:

A beautiful *violet color,* changing quickly to *yellow* and *red,* indicates *strychnine.*

Notes. As the foregoing scheme is intended partly for the benefit of students, I add some notes regarding the chemistry involved in its construction.

Step I.—When organic salts of the alkali metals are ignited, they leave their carbonates, which affect red litmus paper; the the qualitative reactions then separate the two.

Step II.—This introduces the qualitative reaction for ferrous and ferric iron.

Step III.—This depends upon the fact that compounds containing ammonium give off ammonia when brought in contact with an alkali hydroxid. In addition, this step plays the rôle of precipitating the iron as a hydroxid, thus making it possible to operate with a colorless filtrate in Step IV. It then goes farther by rendering Step V assistance by precipitating the alkaloids and keeping them in the iron magma until the time arrives to proceed with their identification. The alkaloidal salts when treated with an alkali give up their acid and, being insoluble in the solution, they precipitate. Upon this

fact the process depends. It is easy to see that the alkaloids remain on the filter, while the acidulous radicals appear as potassium salts in the filtrate.

Step IV.—The rationale of this step is simple. The object of adding acetic acid is to prevent the precipitation of calcium citrate in the cold. This is made necessary through the fact that pyrophosphates (most "iron pyrophosphates" are citro-pyrophosphates) produce with calcium-chlorid test solution a precipitate insoluble in acetic acid, whereas the citrate precipitate is soluble; if therefore acetic acid is first added, the citrate remains unaffected until the solution is boiled. Therefore if a precipitate forms in the cold, filter and test the filtrate as directed. Unless there be an excess, the citrate precipitate does not form in the cold, but calcium citrate, being insoluble in hot solution, precipitates when the solution is boiled.

If the filtrate containing potassium hydroxid also contains a tartrate, the addition of acetic acid produces potassium acid tartrate which is practically insoluble in water, and totally insoluble in alcohol.

Phosphates produce with magnesia mixture the white crystalline ammonio-magnesium phosphate and as pointed out by Nagelvoort (Am. Journ. Pharm., 1895, page 210) an excess of magnesia mixture is objectionable and apt to lead to erroneous conclusions. The magnesia mixture is prepared in the course of the process, acting upon the suggestion of Steiglitz (Am. Journ. Pharm., 1891, page 583), as follows: The filtrate containing potassium hydroxid has added to it ammonium-chlorid solution, whereupon, as shown in a previous reaction, ammonium hydroxid is generated. There remains, however, enough ammonium chlorid in the solution to prevent precipitation of magnesium hydroxid when the magnesium-sulfate solution is added. Having subjected the sample to the test and obtaining what gives every evidence of being a phosphate, the reaction with silver nitrate acts in a confirmatory manner. Orthophosphates give with this reagent a yellow precipitate and pyrophosphates

a white one. The separation of the pyrophosphate from the phosphates is made possible in this step as a result of the fact pointed out by Fresenius, that pyrophosphates produce with magnesium sulfate a precipitate of magnesium pyrophosphate soluble in excess of magnesium sulfate and not precipitated by ammonium hydroxid, which, being the contrary of the behavior of orthophosphates, serves to separate the two acids. The filtrate from the phosphate precipitate, or the solution in which the reagent has produced no effect, is then acidified with acetic acid and heated to boiling: a white flocculent precipitate indicates a pyrophosphate.

Step V.—The fact upon which this step is based has been partly explained in Step III., where the alkaloids remained in the magma, and being soluble in chloroform, that solvent, after being thoroughly shaken with the residue, takes them up. By treating the residue with hot water containing a few drops of diluted sulfuric acid, the sulfates of the alkaloids are formed, and being more soluble in hot water than in cold, the process directs that condition. Mayer's reagent precipitates all the alkaloids included in the scheme, and if no reaction occurs, their absence is safely reported.

The test for quinine is made with Labarraque's solution, and as this is a new method a word regarding it will not be amiss. Every one who has had occasion to qualitatively test for quinine with chlorine or bromin water must know the difficulties encountered through the inconvenience of obtaining either of the above two reagents in a condition to be depended upon. The Labarraque's solution is always at hand. The chemistry concerned in the reaction is easily understood: The Labarraque's solution coming into contact with the acid of the solution under examination has its chlorin liberated, which, if quinine is present, forms with it and a few drops of ammonia the characteristic thalleoquin—shown by an emerald-green-colored solution. Having in many qualitative quinine determinations applied the test as above directed, with the

most satisfactory results the writer has no hesitation in advocating its use in preference to the others referred to.

It might be of interest to here mention that quinidine also gives a green color with this test, but as its higher price precludes any possibility of its ever being substituted for quinine, it is unnecessary to point out the method of differentiation.

The cinchonidine reaction is dependent upon the fact that sodium and potassium tartrate (Rochelle salt) produces with it the insoluble cinchonidine tartrate. Quinine behaves in a similar manner towards this reagent, but the identification in solution 2 of this step eliminates that source of error. If necessary, the alkaloid can in the event of a doubt be further identified as directed.

Cinchonine is identified by its behavior towards ether. Potassium hydroxid precipitates it; ether is added and the cinchonine being insoluble, remains as a white bulky precipitate.

In another portion of the residue the strychnine is identified. The reaction is characteristic, and if applied as directed will detect minute quantities.

The entire process is simple, accurate, inexpensive to operate, quickly carried out, and has everything to commend it.

94. A SCHEME FOR THE DETECTION OF POISONS.

Divide the suspected sample into 3 parts, A, B, and C, and treat as follows:

A. (1) If a liquid, place in a capsule, and on a water-bath evaporate to a syrupy consistency

(2) If a solid, chop up or cut up with scissors into smallest possible pieces.

(3) Transfer product of either (1 or 2), to a flask provided with a reflux (upright Liebig's) condenser or a long tube drawn through the cork of flask. Cover the substance with twice its bulk of a 1% solution of tartaric

acid in alcohol, and heat on a water-bath for one hour (Stas-Otto).

(4) Remove from the water-bath, cool, filter, and carefully concentrate the filtrate on a water-bath until all the alcohol is dissipated.

(5) Filter the concentrated extract through a wetted filter and again evaporate on water-bath to a syrupy consistency.

(6) Dissolve the syrupy extract in absolute alcohol, stirring carefully to aid in effecting as complete a solution as possible. Filter once more, and again drive off the alcohol on the water-bath.

(7) Dissolve the residue from (6) in distilled water, render alkaline with sodium hydroxid, pour into a separatory funnel, and extract it with ether, making at least two extractions.

(8) Divide the ethereal extract from (7) into two portions, each contained in an evaporating dish, and allow the ether to volatilize spontaneously; the alkaloids, strychnine, and veratrine should be tested for according to Chart 89, Steps 2 and 3, respectively, in one of the dishes, and in the other atropine and cocaine should be tested for according to Step 2.

(9) The residue from the separatory funnel is poured into an evaporating dish, NH_4OH added until ammoniacal, and placed on a water-bath, heating it until all the remaining ether is dissipated, and then set aside for 12 hours.

(10) After 12 hours, warm the product of (9), pour into a separatory funnel, and extract it with amylic alcohol. The amylic alcohol extract is carefully evaporated in a porcelain capsule and morphine, identified as in Step 1, Chart 89.

B. (1) Stir this portion prepared just as in A (1) and (2), with about 200 cc. of distilled water, and acidify (if

alkaline or neutral, not otherwise) with 1 or 2 cc. HCl (C. P.).

(2) Place the solution prepared as in (1) on a dialyzer and float it in a liter of distilled water contained in a porcelain vessel.

(3) After 24 hours, concentrate the water in the porcelain dish by evaporation on a water-bath. (This method separates from amorphous organic matter any crystalloid substance, be it inorganic or organic.)

(4) Divide the dialyzed extract (evaporated to about 50 cc. in (3)) into two equal portions.
Test 1st portion for As, Hg, Sb, Zn, Pb, with H_2S.
Test 2d portion for Phenol, Chloral, Chloroform, Aniline, Nitrobenzene, Hydrocyanic Acid, Acetanilide, Phenacetin and the mineral acids.

C. (1) Prepare as in A ((1) and (2)); place in an evaporating dish, add an equal bulk of strong pure HCl, and warm on the water-bath, from time to time adding a crystal of $KCCO_3$ and replacing water lost on evaporation. Continue until all the organic matter is destroyed, expel chlorin by a higher heat, pass H_2S in the warm solution, and test precipitate, according to the tables, for inorganic substances and the acids (except HCl).

95. A SCHEME FOR URANALYSIS.

Observe:

1. *Quantity* passed in 24 hours. It should be from 1200 to 1500 cc.
2. *Color and transparency.*—Colorless, yellow to brown, clear, cloudy or opaque.
3. *Reaction.*—Acid, alkaline or amphoteric; normal urine is faintly acid.
4. *Specific Gravity.*—Should be 1.015 to 1.025 at 15° C.

5. *Sediment.*—Note its quantity, and examine its character with a microscope.

NOTES: 1. When it is directed to warm the urine do not boil.

2. If not perfectly clear, the urine should be filtered before applying tests. If filtration does not clarify it, add a few cc. of NaOH sol., agitate, and filter; or shake a little talcum powder with the urine and filter.

3. If much albumin is present, it should be removed before testing for sugar.

4. Putrid urine should not be tested for sugar by any reagent containing copper or bismuth.

5. If the quantity of U (abbreviation used in this scheme for urine) is too small to float the urinometer, it may be diluted with an equal volume of water, and the last two figures of the specific gravity of this dilute durine, multiplied by two, or the specific gravity may be taken by a specific-gravity bottle.

6. To calculate the quantity of total solids from the specific gravity, multiply the last two figures of the specific gravity by 2.33. This will give the number of grms. in 1000 cc. of urine. The last two figures also indicate approximately the number of grains in a fluid ounce. Full details regarding this relationship between the specific gravity and the amount of total solids may be found in Bartley's Clinical Chemistry.

ORGANIC CONSTITUENTS (Abnormal):

(1) **Albumin.**

(*a*) *Heat Test.*—Add 10 drops of strong acetic acid to 10 cc. of U. Heat; cloudiness or precipitate, if any, indicates albumin.

(*b*) *Nitric-Acid Test.*—Put 2 cc. of colorless HNO_3 into a test-tube, incline the tube, and add slowly, by means of a pipette, 4 cc. of U.

A sharp white band (zone) at point of contact indicates albumin.

Precautions.

1. Mixed urates if present in excess will also give a band higher up. It is dissipated by warming (not boiling).

2. After the administration of resinous drugs (copaiba, etc.) or turpentine, a yellowish clouded zone also forms, which is redissolved by alcohol (albumin zone does not dissolve).

(*c*) *Picric-Acid Test.*—Mix equal volumes of saturated solution of picric acid and U, shake and warm; any remaining ppt. is albumin.

Precaution.

Picric acid precipitates also urates, peptones, and vegetable alkaloids, which redissolve on warming.

(*d*) *Tanret's Test.*—Acidify 5 cc. of U with acetic acid, add Tanret's reagent drop by drop until 2 cc. have been added. Then warm. Any ppt. remaining is albumin.

Precaution. Same as under (*c*).

(*e*) *Potassium-Ferrocyanid Test.*—Acidify 4 cc. of U with acetic acid, add 2 cc. of a saturated soluti n of K_4FeCy_6; any precipitate is albumin.

(*f*) *Quantitative Estimation.*—Fill an Esbach albuminometer to the letter "U" with urine, and then to the letter "R" with Esbach's reagent. Cork securely, shake well, and set aside for 24 hours, agitating once or twice during that time—then read. Each one of the main divisions read off indicates 1 grm. of albumin in a liter of urine.

(2) **Peptones.**

(*a*) *Ralfe's Test.*—Place 4 cc. Fehling's reagent in a test-tube, and gently overlay with urine. At point of contact a zone of phosphates forms; above this

another rose-colored zone, or "halo," will float if peptone is present.

If mixed with albumin the halo will be purple.

(*b*) *Randolph's Test.*—To 5 cc. of faintly acid urine add 4 drops of a saturated solution of KI and 4 drops of Millon's reagent. If peptones or bile acids are present, a yellow ppt. falls. Test for bile acids; if these be absent, the yellow ppt. indicates peptones.

(3) **Glucose** (Sugar).

(*a*) *Fehling's Test.*—Place 5 cc. of Fehling's reagent in a test-tube, dilute with 5 cc. water and heat to boiling. Add now drop by drop 5 cc. of urine, heating after each addition. A yellow or orange coloration or a brick-red ppt. of copper suboxid (Cu_2O) indicates glucose.

(*b*) *Pavy's Test.*—Place 5 cc. of Pavy's reagent in a test-tube and warm. Now add 5 cc. of U; a partial or a total disappearance of the blue color indicates sugar.

(*c*) *Haine's Test.*—Heat 5 cc. of Haine's reagent in a test-tube to boiling. Drop by drop add half a cc. of U, and boil again; any turbidity, or an orange-red ppt. of Cu_2O, indicates glucose.

(*d*) *Böttger's Bismuth Test.*—Place in a test-tube 3 cc. of U, 1 cc. of solution of Na_2CO_3 and a little (0.3 grm.) bismuth subnitrate; boil these together for 2 minutes. If sugar be present in quantity, black metallic bismuth deposits; if a small quantity only is present the sol. will assume a grayish color.

(*e*) *Nylander's Test.*—Boil together in a test-tube 10 cc. of U with 1 cc. of Nylander's reagent. If a light-gray or black precipitate forms it indicates glucose.

(*f*) *Indigo-Carmine Test.*—Place 4 cc. of a freshly prepared solution of indigo carmine in a test-tube, add half of a cc. of Na_2CO_3 solution and boil together; the

color should persist; if it does not, add another cc. of the indigo-carmine solution (caustic alkalies discharge the color of indigo carmine). Add now 3 drops of U, and without agitation warm 1 minute. If glucose be present the color changes to purple, red and finally straw-yellow. Now shake the tube and the colors recur in the reverse order.

(*g*) *Quantitative Estimation* (by Fermentation).—Take $\frac{1}{10}$ part of a cake of Fleischmann's yeast, shake thoroughly with 10 cc. urine, pour into an Einhorn saccharometer, and set aside for 24 hours in a room of ordinary temperature (25° C. = 77° F.). Read off the percentage of glucose present.

(*h*) *Quantitative Estimation* (with Fehling's Reagent).—Place in a 200-cc. flask 10 cc. of Fehling's solution; to this add 10 cc. of a freshly prepared 10% solution of K_4FeCy_6 and 30 cc. of water. Heat the mixture on a water-bath (best temperature for the operation being between 80° and 90° C.); the U, diluted if it contains much sugar, is then run in drop by drop until the blue color just disappears. Excess of glucose added quickly turns the solution yellowish-brown (copper ferrocyanid forms). This is Prof. Bartley's method and is both reliable and rapid.

(4) **Indican** (Uroxanthin).

(*a*) Place 4 cc. of HCl in a test-tube, add 3 drops HNO_3, and agitating constantly add drop by drop 10 to 20 drops of urine. If indican is present in normal quantity, the solution will be colored delicate yellowish red; if in excess, the solution is colored red to violet.

Precaution.

If biliary acids are present, remove them before testing for indican by adding to 10 cc. of U 8 drops

of $Pb(C_2H_3O_2)_2$ solution and filtering. The filtrate is now tested for indican.

(*b*) Place in a test-tube 4 cc. each HCl and U, agitate, add 2 or 3 drops of dilute (1 : 3) solution of chlorinated soda, and shake; a reddish-blue or bluish-black coloration indicates indican (indigo is formed in this reaction; a weak solution of NaClO is directed, as an excess would bleach the indigo). If now 2 cc. of $CHCl_3$ be added and the mixture agitated, the indigo is dissolved out and with the chloroform settles at the bottom as a blue layer (the depth of the blue color is indicative of the quantity of indican present).

(5) **Blood.**

(*a*) *Heller's Test.*—To 5 cc. of U contained in a test-tube add 2 cc. of KOH solution and warm.

The earthy phosphates which precipitate carry with them the blood coloring-matter, and if blood is present the precipitate will be blood-red, in absence of blood, white.

(*b*) *Almén's Test.*—Shake together in a test-tube 5 cc. each of tincture guaiacum and hydrogen dioxid (or old resinified turpentine oil), and drop by drop add about 5 cc. of U. Let stand a few minutes; if blood is present, a blue or bluish-green coloration is formed in the upper layer. If much blood is present, on agitating the tube it will diffuse through the entire liquid, giving it a creamy-bluish color.

(6) **Bile.**

(*a*) *Heller's Test* (for Bile Pigments).—Put 6 cc. of HCl in a test-tube and drop in just enough of the U to color it. Underlay this mixture with pure HNO_3. A play of colors at point of contact indicates biliary pigments.

(*b*) *Fleishl's Test.*—Underlay a mixture of 5 cc. each strong HNO_3 and U, with strong H_2SO_4. A play of

colors from rose to purple and green at point of contact indicates bile.

(c) *Iodin Test.*—Upon the surface of 5 cc. of U, carefully float 10 drops of tincture of iodin. At the point of contact an emerald-green zone is formed if bile is present.

(d) *Pettenkofer's Test* (for Biliary Acids).—Add to 5 cc. U contained in a test-tube 4 drops of a solution of cane-sugar (saccharose 1:3), shake, and carefully underlay with strong H_2SO_4. Let stand for a few minutes; if biliary acids be present, a purple band is formed at point of contact.

(e) *Oliver's Peptone Test* (for Biliary Acids).—Clarify the U by filtration, and dilute to the sp. gr. of 1.008. Place in a test-tube 4 cc. of Oliver's reagent and run into it 1 cc. of the U, diluted as above. If biliary acids are present, a distinct milkiness promptly appears, which becomes more intense after a few minutes. Oliver's reagent is composed of pulverized peptone, 2 grm.; salicylic acid, 0.25 grm.; acetic acid, 2 cc.; and sufficient distilled water to make 250 cc.

Precaution.

The above test is very delicate and reliable, but only in the absence of albumin, which should be removed by boiling the U with a few drops of $HC_2H_3O_2$ and filtering.

(7) **Acetone.**

(a) *Legal's Test.*—Pour into a test-tube 2 cc. of a strong freshly prepared solution of sodium nitroprusside, and add 4 cc. of U and 2 cc. NaOH solution. The mixture acquires a red coloration, which may be due to creatinin (a normal constituent of U) as well as to acetone. Add 6 or 8 cc. of glacial $HC_2H_3O_2$; if the mixture now assumes a claret-red or violet

color, acetone is present in considerable quantity; if the color is discharged by the acid, it was due to creatinin only.

(*b*) *Lieben's Test.*—Pour into a test-tube 6 cc. of U, add 10 drops solution of iodin and about 1 cc. of NH_4OH, and heat. If acetone be present, crystals of iodoform will form and deposit; the iodoform may be recognized by its characteristic aromatic odor.

ORGANIC CONSTITUENTS (Normal):

(1) **Urea** (Carbamid, CH_4N_2O), *Quantitative Estimation of.*

(*a*) Fill a *Doremus* ureometer to the double mark with hypobromite solution (made by dissolving 100 grm. of NaOH in 250 cc. of water, and to this adding 25 cc. of bromin), then add enough water to half fill the bulb. Now add 1 cc. of U by means of a nipple-pipette, forcing it as far up into the graduated cylinder as possible, stopper securely, let stand 15 minutes or until all the nitrogen is evolved, then read off.

(*b*) *Gas-tube Method of Bartley.*—Pour into the gas-tube a 20% KBr solution up to the fifth division and chlorinated-soda solution to the twentieth division; the tube is now inclined, carefully overlayed with 5 cc. of distilled water, and 1 cc. of U carefully measured is added from a nipple-pipette, carefully avoiding its mixing with the reagents. The thumb of the right hand is now tightly pressed over the opening of the tube, which is firmly held in both hands and slowly inverted (carefully avoiding violent agitation) until reaction is complete (in from 2 to 4 minutes). Now invert the gas-tube, make a careful reading, and thus inverted open it under water contained in a broad, deep vessel and again read off.

The difference between the first and second readings

equals the number of cc. of nitrogen evolved. Each cc. of $N = 0.0027$ grm. of urea in 1 cc. of U.

(2) **Urohæmatin,** *Hartley's Test.*—Dilute the total U collected in 24 hours with distilled water till it measures 1.8 L; if the amount for 24 hours exceeds this figure, concentrate it to this quantity. Take 8 cc. of the so prepared U, add 2 cc. of pure strong HNO_3, and let stand for some time. If urohæmatin is present in normal quantities only, a slight change of color will be seen, but if present in excess, the liquid will become pink, red, crimson, or purple in color, according to the quantity present.

(3) **Vegetable Coloring Matter.**

(*a*) Observed in alkaline urines having a red or reddish-brown color. Add HCl: the urine will turn yellow. Add an excess of NH_4OH: the urine again assumes a reddish color.

(*b*) *Test for Urobilin.*—To 5 cc. of U add 2 cc. NH_4OH: the urine will assume a greenish hue. Filter, to the filtrate add 2 cc. of a 1% solution of $ZnCl_2$, and shake. A rose-red color with greenish fluorescence is due to urobilin.

(4) **Uric Acid,** $C_5H_4N_4O_3$.

(*a*) *Murexid Test.*—Evaporate 10 cc. of U to dryness in a porcelain capsule, and then add a drop or two of HNO_3 to dissolve the residue. Dissipate the uncombined HNO_3 by heating on a water-bath. When dry, moisten the residue with 1 or 2 drops of NH_4OH. A purple-red color of *murexid* indicates uric acid.

INORGANIC CONSTITUENTS:

(5) **Chlorids.**—*Approximate Estimation.*

(*a*) Add 2 drops of strong HNO_3 to 5 cc. of U contained in a test-tube and mix well (HNO_3 keeps phosphates in solution); add now 1 drop of a 1:8 solution of

$AgNO_3$. If the U contains 0.5% of chlorids, they will be ppd. as cheesy lumps, which do not further break up or render the urine more milky by moving the tube about.

If the U contains 0.1% or less of chlorids, no cheesy lumps will appear, but a simple cloudiness is uniformly diffused through the entire liquid.

Precaution.

If much albumin be present in the U, it should be removed before applying above test.

(*b*) *Quantitative Estimation.*—Dilute 10 cc. of U with 40 cc. of distilled water, add 10 drops of 10% potassium-chromate solution (free from chlorids), and from a burette run in drop by drop tenth normal $AgNO_3$ solution, until a permanent reddish-brown color of silver chromate is produced, indicating end-reaction. Each cc. $\frac{N}{10}$ $AgNO_3$ solution = 0.00584 grm. of chlorids, calculated to NaCl.

(6) **Phosphates** (1. Earthy).

(*a*) Add to 5 cc. of U 3 cc. of NH_4OH; the earthy phosphates are precipitated.
These may be separated by filtration, dried at a low heat, and weighed—if required.

(*b*) (2. Alkaline). *Approximate Estimation.*—Filter out the earthy phosphates as precipitated in (*a*), and to the filtrate contained in a test-tube add $\frac{1}{3}$ its own volume of magnesia mixture. If the entire fluid presents a cloudy appearance or a milkiness, the alkaline phosphates are normal. If, however, a decided, dense, milk, or cream-like precipitate forms, the alkaline phosphates are present in greater than normal quantities.

If the fluid is but very slightly cloudy, transmit-

ting light, the phosphates are present in less than the normal quantities.

(7) **Sulfates.**—These are usually reported as potassium indoxyl-sulfate (indican). An *approximate method* for the estimation of sulfates is the following: To 6 cc. of U contained in a test-tube add 8 drops of HCl; the mixture is shaken and 2 cc. of $BaCl_2$ added. An opaque milky cloudiness indicates that the sulfates are present in normal quantity.

If the opacity is intense, the whole mixture presenting a creamy appearance, the sulfates are present in excess above the normal quantity.

If the cloudiness is so slight as to transmit light, the quantity of sulfates is subnormal.

Microscopical Examination.—Besides the chemical examination as given in the above scheme, a microscopic examination of the sediment should likewise be made. The more important constituents revealed in this way are the following:

(*a*) *Epithelium,* whether single cells or squamous masses are present.

(*b*) *Crystals* of uric acid, triple phosphates, calcium oxalate, cystin plates, etc.

(*c*) *Amorphous deposits* of urates, broken-up cellular structures, detritus, etc.

(*d*) *Blood,* discs and casts.

(*e*) *Pus,* single cells and sacs.

(*f*) *Casts* (tube, waxy, hyaline, granular, epithelial, etc.)

(*g*) *Mucous,* cells and casts.

Also, *Fungi, Bacteria,* and *Spermatozoids* are sometimes reported.

Report.—The findings of a urinalysis may be reported according to the following scheme used by the authors:

New York, ...190.

REPORT ON URANALYSIS.

When Received. . . . .
Dr. . . . . *Patient*. . . . .

PHYSICAL EXAMINATION.

Odor	Color
Spec. Gravity	Reaction
Appearance	
Sediment	
Quantity passed in 24 hours	

CHEMICAL ANALYSIS.

Albumin
Sugar
Urea
Bile
Acetone
Indican
Chlorids
Phosphates

MICROSCOPICAL EXAMINATION,

Epithelium
Crystals
Amorphous Deposits
Blood
Pus
Casts
Mucous
Fungi
Spermatozoa
Bacteria

Analyst.

PREPARATION OF REAGENTS.

Reagents should be prepared only from chemically pure substances, or, better, such as are guaranteed as to their purity and strength, e.g., "Merck's Guaranteed Reagents." The success of the analytic operations depends very largely on the purity of reagents.

The water used in the preparation of reagents should be freshly distilled and tested for impurities.

ACIDS.

When "acids" are mentioned in the text, dilute acids are meant unless otherwise specified.

When "strong" or "concentrated" acids are mentioned use the undiluted acids of the strength specified by the U. S. P.

HCl,	1 part to 4 parts H_2O by volume.
H_2SO_4,	1 " " 4 " H_2O " "
HNO_3,	1 " " 5 " H_2O " "
Aqua Regia HNO_3,	1 " " 3 " HCl " "

SALTS.

Parts by Volume.

$(NH_4)_2CO_3$,	1 part to 8 parts H_2O, add 1 part NH_4OH.
$(NH_4)_2C_2O_4$,	1 " " 24 " H_2O
NH_4Cl,	1 " " 10 " H_2O
KOH,	1 " " 10 " H_2O
$NaOH$,	1 " " 10 " H_2O
K_2CrO_4,	1 " " 10 " H_2O
$K_2Cr_2O_7$,	1 " " 10 " H_2O
K_3FeCy_6,	1 " " 15 " H_2O
K_4FeCy_6,	1 " " 15 " H_2O

Na_2CO_3,	1 part	to	10	parts	H_2O
Na_2HPO_4,	1 "	"	10	"	H_2O
$BaCl_2$,	1 "	"	10	"	H_2O
$HgCl_2$,	1 "	"	20	"	H_2O
$AgNO_3$,	1 "	"	20	"	H_2O
$Pb(C_2H_3O_2)_2$,	1 "	"	10	"	H_2O
$MgSO_4$,	1 "	"	8	"	H_2O
$Co(NO_3)_2$,	1 "	"	10	"	H_2O
$(NH_4)MoO_4$,	1 "	"	4	"	NH_4OH(strong), add 15 parts HNO_3(34%)
KCy,	1 "	"	10	"	H_2O
KI,	1 "	"	25	"	H_2O
$FeSO_4$,	2 "	"	10	"	add H_2SO_4 a few drops.
$(NH_4)_2SO_4$,	1 "	"	10	"	H_2O
$H_2C_4H_4O_6$,	1 "	"	20	"	H_2O
$Ba(OH)_2$,	1 "	"	20	"	H_2O
$BaSO_4$,	a saturated solution.				
$CaSO_4$,	" " "				
$NaHC_4H_4O_6$,	" " "				

GASES.

H_2S.—Generate the gas from FeS by a dilute H_2SO_4 (1 p. acid to 12 p. water).

NH_4HS.—Pass H_2S in a slow current into some pure NH_4OH until the latter is saturated. This solution is sometimes called yellow ammonium sulfid.

$(NH_4)_2S$ solution is made by mixing 3 parts of the foregoing with 2 parts of ammonia-water.

SPECIAL REAGENTS.

Fe_2Cl_6.—1 part to 10 parts H_2O by volume.
KSCy.— 1 " " 10 " " " "
$NaC_2H_3O_2$.—A saturated solution.

$NaClO_2$—Mix 3 grm. of bleaching-powder (chlorinated lime) with 3 grm. of Na_2CO_3 (anhydrous) and dissolve in 400 cc. of distilled water. Let settle, and decant the solution.

Bromin-water.—Add some Br to water, agitate, allow to stand and decant for use.

Ether.—U. S. P. ether.

Alcohol.—U. S. P. alcohol 95%.

Copper sulfate.—1 part to 10 parts H_2O.

Tannic acid.—1 part to 100 parts H_2O.

Dimethyl-amido-azo-benzene.—1 grm. to 200 cc. C_2H_5OH.

Indigo-carmine.—10% solution.

Alphanaphthol.—15 parts to 100 parts C_2H_5OH.

Picric Acid.—A saturated solution in water.

Magnesia Mixture.—1 part $MgSO_4$ cryst.,
2 parts NH_4Cl,
4 parts NH_4OH,
8 parts H_2O.

Nessler's Reagent.—(1) Dissolve 35.0 grm. KI in 100 cc. H_2O. (2) Dissolve 17.0 grm. $HgCl_2$ in 300 cc. H_2O.

The liquids may be heated to aid solution, but if so, they must be cooled before mixing. Pour the second solution into the first until a permanent ppt. is produced, then dilute with 20% NaOH solution to 1000 cc.; agitate and again add enough of solution (2) until a permanent ppt. forms. Allow to stand till settled, and decant the clear portion for use.

Millon's Reagent.—1 p. metallic Hg by weight, and 2 p. HNO_3 (strong) by weight; gently warm until all Hg dissolves, and dilute with 6 p. H_2O.

Nylander's Reagent.—4 grm. Rochelle salt, 2 grm. $BiONO_3$, a 10 grm. NaOH (dissolved in 90 cc. water). Mix, and keep in a dark bottle in the dark.

Gunzberg's Reagent.—1 grm. vanillin, 2 grm. phloroglucin, and 100 cc. alcohol.

Froehde's (or Fröhde's) Reagent.—1 grm. sodium molybdate 10 cc. H_2SO_4 (strong).

Fusing Mixture.—1 p. Na_2CO_3 and 3 p. KNO_3.

Iodin Solution.—1 grm. I, 2 grm. KI, and 300 cc. H_2O.

Esbach's Reagent.—10 grm. picric acid, 20 grm. citric acid, and water to make 1000 cc. of finished product.

Fehling's Reagent.—(1) 34.64 grm. $CuSO_4$ (crystal). Dissolve in water and make up to 500 cc.

(2) 173 grm. Rochelle salt, and 125 grm. NaOH. Dissolve in water and make up to 500 cc. The solutions are to be kept separately, and mixed together in equal quantities just before use.

Diazo Reagent.—(1) 2 grm. sulfanilic acid, 50 cc. HCl (strong) and H_2O to make 1000 cc. of finished product.

(2) 5 grm. $NaNO_2$. Make up to 1000 cc. with water.

Dragendorff's Reagent.—1.5 grm. $BiONO_3$, boil with 20 cc. H_2O, add 7 grm. KI, shake, and add 20 drops HCl (dilute).

Mayer's Reagent.—1.35 grm. $HgCl_2$, dissolved in 50 cc. water; then add 5 grm. KI dissolved in 50 cc. H_2O, and mix the two solutions.

Haine's Sugar Test.—2 grm. $CuSO_4$, dissolve in 15 cc. H_2O, add 15 cc. glycerin, mix well, and add 150 cc. solution KOH (U. S. P., 1890).

Tanret's Reagent.—(1) 1.35 grm. $HgCl_2$, dissolved in 30 cc. H_2O (hot).

(2) 3.32 grm. KI, dissolved in 30 cc. H_2O.

Mix the solutions 1 and 2, add 20 cc. acetic acid, and make up to 100 cc. with H_2O.

"Euchlorin."—Place in a test-tube 0.2 grm. of $KClO_3$, add to it 4 drops HCl (strong), and when Cl gas is evolved dilute with H_2O to 30 cc.

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